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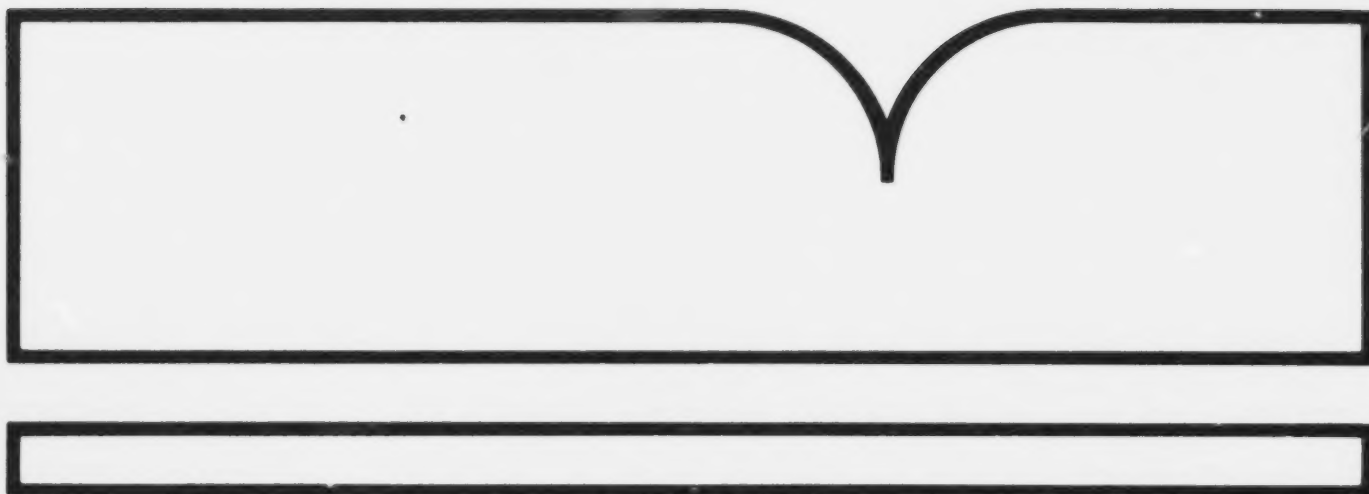
Rate of Flow of Leachate through Clay Soil Liners

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**RATE OF FLOW OF LEACHATE
THROUGH CLAY SOIL LINERS**

by

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This report documents the time of travel of solutes through laboratory-compacted clay soils. These data define the effects of physical and geochemical parameters -- low hydraulic gradient and diffusion -- that control solute transport. This information will be useful to those involved in policy development, research, and design of soils compacted for service as waste management system liners or infiltration barriers in cover systems.

ABSTRACT

The objective of this research was to measure the time of travel (TOT) of inorganic solutes through laboratory columns of compacted clay, to determine the physical and geochemical parameters that controlled solute transport through the soil columns, and to compare measured and predicted TOT's. Two clay soils were used: kaolinite (a low-plasticity, commercially-produced clay) and Lufkin clay (a highly plastic, naturally-occurring clay soil). Anionic tracers were chloride and bromide; potassium and zinc were the cationic tracers.

Diffusion cells were designed, constructed, and used to measure the effective diffusion coefficient of the tracers in the two soils. Diffusion coefficients for anions were typically $6-7 \times 10^{-6} \text{ cm}^2/\text{s}$ for kaolinite and $1-15 \times 10^{-6} \text{ cm}^2/\text{s}$ for Lufkin clay; somewhat lower values were determined for cations.

Column tests were used to determine the effective porosity ratio, which is defined as effective porosity divided by total porosity. The effective porosity is equal to the volume of the void space that conducts most of the fluid flow divided by the total (bulk) volume of the soil. The effective porosity ratio increased with increasing hydraulic gradient in kaolinite from a low of about 0.25 at a gradient of 1 to a high of 1 at a gradient of 20. With Lufkin clay, the effective porosity ratio was between 0.02 and 0.16. Breakthrough times were controlled more by the low effective porosities than by molecular diffusion.

The computer program SOILINER predicted times of travel that were larger than actual TOT's by a factor of up to 52. The failure to account for effective porosity ratios less than 1 was the cause for the poor predictions from SOILINER.

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LIST OF SYMBOLS

A	cross-sectional area of flow
a	length of soil used in diffusion test
a_L	longitudinal dispersivity
c	concentration
c_0	constant concentration in influent liquid
D	diffusion coefficient
D_d	hydrodynamic dispersion coefficient
D_0	free-solution diffusion coefficient
D^*	effective diffusion coefficient
H	height of liquid ponded above liner
h_p	pressure head
i	hydraulic gradient
J_a	advective mass flux
J_d	diffusional mass flux
K_d	distribution coefficient (S/c)
k	hydraulic conductivity
L	thickness of liner
l	height of solution in diffusional cell reservoir
n	porosity
n_e	effective porosity
p	suction head
Q	quantity of flow
q	rate of flow (Q/t)
S	mass of solute sorbed per mass of soil

LIST OF SYMBOLS (Continued)

t	time
TOT	time of travel of a constituent through a soil liner
v	flux (q/A)
v_s	seepage velocity
x	direction
τ	tortuosity factor
θ	volumetric water content

SECTION 1

INTRODUCTION

BACKGROUND

In 1985, the United States Environmental Protection Agency (EPA) published a draft document entitled "Minimum Technology Guidance on Double Liner Systems for Landfills and Surface Impoundments" (EPA, 1985). The document establishes requirements for lining systems at land disposal units for hazardous waste.

Two designs for double lining systems are described in the EPA technical guidance document. The first design, shown schematically in Figure 1.1, includes a primary flexible membrane liner (FML) and a composite secondary liner. The composite secondary liner consists of an FML overlying a compacted soil liner. The EPA technical guidance document states that the soil liner component should be designed, operated, and constructed to minimize the migration of any constituent of the waste liquid through the upper component if a breach in the upper component were to occur. The soil liner should be at least 3-ft thick and consist of compacted, low-permeability soil with an in-place hydraulic conductivity of 1×10^{-7} cm/s or less.

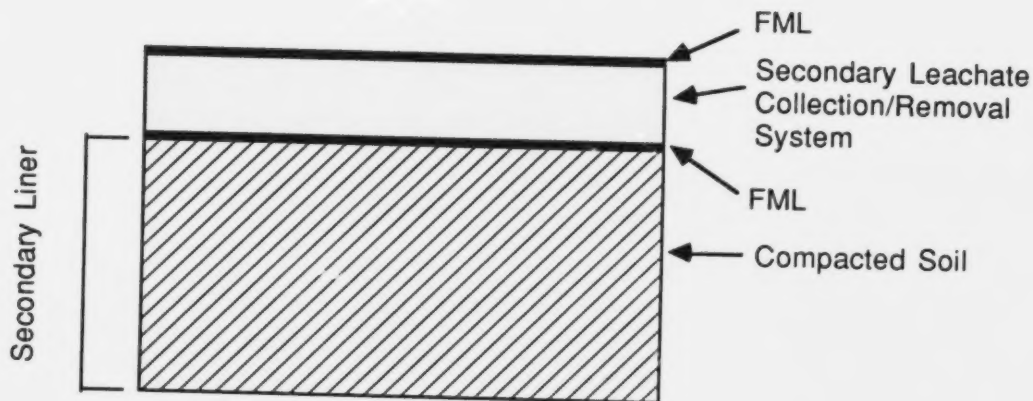


Figure 1.1 Double Liner with Composite Secondary Liner

The second design, shown in Figure 1.2, utilizes a compacted soil liner alone for the secondary liner. The EPA technical guidance document states that this type of secondary liner is designed, operated, and constructed to prevent the migration of any constituent through the liner during the period the facility remains in operation, including a 30-year post-closure monitoring period. The use of the second type of design (without an FML in the secondary liner) requires that the designer determine the time required for chemicals to pass through the liner and to size the liner so that the chemicals will not pass through the secondary liner during the operating life of the facility plus the post-closure monitoring period. To determine whether constituents will pass through the liner during this period, calculations of time of travel (TOT) through the liner are needed. The U. S. EPA has sponsored the development of a computer program, SOILINER (EPA, 1984), for such calculations. Analysis with SOILINER is based on an advection model, which assumes that waste constituents dissolved in leachate or in the waste liquid are carried by flowing liquid. Under realistic conditions, chemicals migrate through soil in a dispersive fashion and mix with water in the soil, but mixing is ignored in SOILINER. Also, molecular diffusion may be an important mechanism driving the migration of constituents through low-permeability soils, but diffusion, like mechanical dispersion (mixing), is ignored in SOILINER.

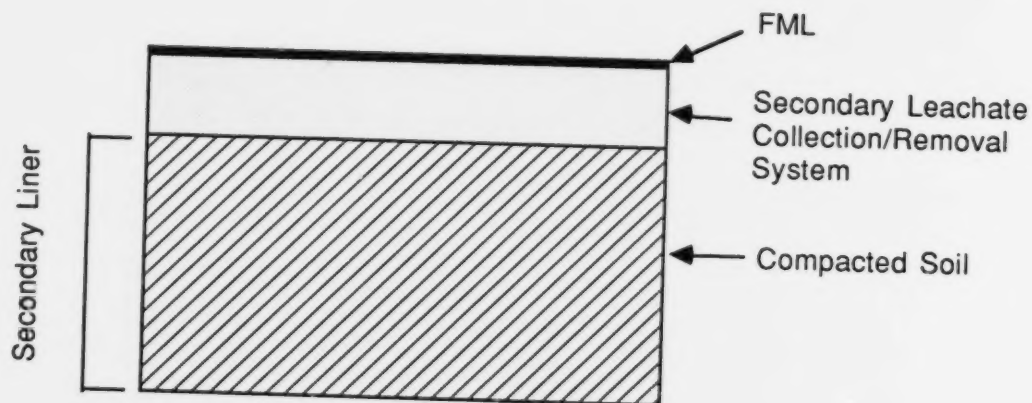


Figure 1.2 Double Liner with Compacted Soil Secondary Liner

OBJECTIVE OF STUDY

The objective of this study was to investigate the transport of inorganic chemicals through compacted clay soils under conditions closely approximating field conditions. The work included laboratory experiments to measure the time of travel of inorganic chemicals through compacted soil and comparisons of predicted and actual times of travel. The research is intended to provide data that will assist in evaluating

existing methodologies for calculating time of travel of waste constituents through soil liners and, ultimately, in developing improved methodologies for such predictions.

Several variables were included in the experimental program. Tests were performed over a range of hydraulic gradient, because the relative importance of molecular diffusion depends on advective velocity, which is proportional to hydraulic gradient. Most tests were performed on soils that were presoaked with water, but some tests were performed on unsaturated soils to provide comparative data and to provide data for analysis with program SOILINER. Two concentrations of chemicals in water, and two soils with different mineralogies, were used to span a range of conditions.

SECTION 2

CONCLUSIONS

The conclusions that can be drawn from this study are as follows:

1. The adsorption of potassium and zinc by kaolinite and Lufkin clay was nonlinear, based on batch adsorption tests. Nonlinear Freundlich and Langmuir isotherms represented the experimentally-determined isotherms well.
2. Lufkin clay, which contains montmorillonite and has a high cation exchange capacity, had a much greater capacity to sorb potassium and zinc than kaolinite, which has a low cation exchange capacity. At low concentration, the distribution coefficient (K_d) for potassium and zinc being sorbed by kaolinite was approximately 0.002 (mg/g)/(mg/L). For Lufkin clay, the K_d values for potassium and zinc at low concentration were approximately 0.01 to 0.1 (mg/g)/(mg/L), which is a factor of 5 (potassium) to 50 (zinc) times higher than for kaolinite. The cation exchange capacities of kaolinite and zinc were found to be 5 and 25 meq/100g, respectively.
3. The effective diffusion coefficient (D^*) for anions (Cl^- and Br^-) diffusing into kaolinite was 6 to $7 \times 10^{-6} \text{ cm}^2/\text{s}$. The free-solution diffusion coefficient for Cl^- is $20 \times 10^{-6} \text{ cm}^2/\text{s}$, and that of Br^- is $21 \times 10^{-6} \text{ cm}^2/\text{s}$. The computed tortuosity factor (τ) for anions diffusing in kaolinite was 0.29 to 0.35, which is within the range reported in the literature for soil.
4. The effective diffusion coefficient for Br^- diffusing in Lufkin clay varied, depending on how D^* was calculated, between 1 and $15 \times 10^{-6} \text{ cm}^2/\text{s}$; the calculated τ ranged from 0.05 to 0.71, which, again, is within the range reported in the literature for soil. The effective diffusion coefficient for Cl^- could not be determined from the tests on Lufkin clay because the Cl^- concentration in the diffusional solution was similar to the Cl^- concentration in the soil water.
5. The effective diffusion coefficients for the cations K^+ and Zn^{2+} diffusing into kaolinite and Lufkin clay were similar to the values for Cl^- and Br^- . Batch adsorption tests indicated strong sorption of cations, particularly in Lufkin clay, but sorption did not have much influence on D^* values.
6. Soils used for column tests swelled when presoaked with the standard wetting solution (0.01 N CaSO_4). Kaolinite swelled 2 to 5%, and Lufkin clay swelled 5 to 20%. The water content and dry density of the soil varied, with highest water content and lowest dry density near the end of the soil column exposed to water. The wetted end was not restrained from swelling.

7. Significant biological growth took place in reservoirs containing tracers used for diffusion and column tests. Green algae were seen in some cells. Black bacteria that likely converted sulfate to metal sulfide were present in some cells. However, a control test indicated little loss of tracers from the permeant solution from micro-biological activity or other possible sinks.
8. The effective porosity of kaolinite and Lufkin clay was calculated from breakthrough curves determined for anions passing through presoaked, essentially saturated soil columns. An analytic advection-dispersion solution was fit to the experimentally-determined breakthrough curves by varying the effective porosity (n_e) and hydrodynamic dispersion coefficient until a best-fit (by eye) was obtained. The effective porosity ratio, defined as the ratio of effective porosity (n_e) to total porosity (n), was found to be between 0.25 and 1.0 for kaolinite and between 0.02 and 0.16 for Lufkin clay. For Lufkin clay, the value of n_e/n was the same at a hydraulic gradient of 20 and 50 and scattered randomly between replicates over the range of 0.02 to 0.16. For kaolinite, the effective porosity ratio was 1 at the highest hydraulic gradient (20) and was lowest (0.25 to 0.3) at the smallest gradient (1) used.
9. Hydrodynamic dispersion coefficients were calculated for anionic tracers passing through presoaked kaolinite and Lufkin clay. The hydrodynamic dispersion coefficients for all but one series of tests (tests on kaolinite at the highest hydraulic gradient, which was 20) were essentially equal to the effective diffusion coefficient. Theoretically, when the hydrodynamic dispersion coefficient equals the effective diffusion coefficient, molecular diffusion is much more important than mechanical dispersion (mechanical mixing of solutes with soil water). For kaolinite permeated at a hydraulic gradient of 20, the hydrodynamic dispersion coefficient was approximately 3 times larger than the effective diffusion coefficient, which indicates that at this relatively high gradient, mechanical dispersion was more important than molecular diffusion.
10. Cationic species (K^+ and Zn^{2+}) migrated more slowly through columns of kaolinite than did Cl^- and Br^- . The retardation factor (which is the ratio of the velocity of the transporting water to the velocity of a solute) was typically in the range of 3 to 10 for cations. The retardation factor determined from column tests for cations differed from values computed from batch adsorption tests by a factor of up to about 2. Differences in chemical equilibrium and soil-solution ratios likely caused the differences between batch and column tests. Data from cations passing through Lufkin clay were difficult to interpret, and retardation factors were not reported from these tests.
11. The importance of molecular diffusion in determining breakthrough times in the column tests was relatively unimportant compared with the importance of small effective porosity. The low values of effective porosity in Lufkin clay ($n_e/n = 0.02 - 0.16$) resulted in breakthrough times of only a few days despite the low hydraulic conductivity ($< 1 \times 10^{-9}$ cm/s) of the soil.
12. Analyses of the movement of tracers through unsaturated soil columns using program SOILINER yielded poor comparisons with experimental results. The breakthrough time predicted by SOILINER was too large by a factor of 2 to 5 for kaolinite and too large by a factor of 9 to 53 for Lufkin clay. The poor predictions of SOILINER were attributed to

the failure of SOILINER to consider molecular diffusion, and (more importantly) the assumption by SOILINER that the effective porosity was equal to the total porosity. If the breakthrough times predicted by SOILINER are multiplied by the experimentally-determined values of n_e/n , good agreement between predicted and measured breakthrough time is achieved.

13. There was no evidence of the existence of a threshold hydraulic gradient in the tests.

SECTION 3

RECOMMENDATIONS

Based on the findings from this investigation, the following recommendations are made:

1. Batch adsorption tests involving soil liner material and leachate should be performed on the actual, or if unavailable, simulated leachate. The batch tests should not be performed on monoionic species because competition between cations for sorption sites on the soil will lead to different distribution coefficients than measured with solutions containing more than one ion.
2. Batch adsorption tests can provide an indication of retardation coefficient for cations migrating through soil liners, but precise agreement between retardation coefficients determined from batch and column tests cannot be expected due to different geochemical conditions and soil-solution ratios. Until field data are developed, it cannot be determined whether either batch adsorption tests or laboratory column tests provide retardation coefficients that accurately reflect field values.
3. The effective diffusion coefficient can be affected by many geochemical parameters and is difficult to measure accurately. Conservative (somewhat high) values of effective diffusion coefficient can be estimated by multiplying the free-solution diffusion coefficient for a chemical by the tortuosity factor, τ . Values of τ measured in this study ranged from 0.05 to 0.71, with many falling in the range of 0.3 to 0.4. A conservative value of $\tau = 0.7$ is recommended, unless actual diffusion tests are performed on the solute(s) of interest to measure directly the effective diffusion coefficient. Although cations should diffuse more slowly than anions through soil liner materials (due to cation exchange and other sorption processes), little direct evidence of significantly reduced diffusion rates for cations was seen in this study. If actual data on the effective diffusion coefficient of a cation are lacking, it is recommended that the diffusion coefficient of the cation be assumed to be the same as that of a conservative tracer such as Cl^- or Br^- , both of which have free-solution diffusion coefficient of approximately $20 \times 10^{-6} \text{ cm}^2/\text{s}$.
4. The breakthrough time of solutes passing through columns of compacted clay is influenced significantly by the effective porosity of the soil. The ratio of effective porosity to total porosity (n_e/n) was found to be between 0.02 and 1, which is a very large range, for the soils and hydraulic gradients used in this study. It is recommended that column tests using a nonreactive tracer, e.g., Br^- , be used to determine effective porosity for a given soil compacted to a given water content and dry density. The range of effective porosities measured in this study is too large to enable one to estimate effective porosity reliably. Column tests used to determine effective porosity should be conducted at a hydraulic gradient that is as close to the field value as possible.

5. The computer program SOILINER is not recommended for calculation of time of travel of a constituent through a compacted soil liner unless the effective porosity ratio is close to unity. It is recommended that this program be revised to account for molecular diffusion, for mechanical dispersion, and (most importantly) for effective porosity less than the total porosity.

SECTION 4

MOVEMENT OF INORGANIC CHEMICALS THROUGH SOIL LINERS

MECHANISMS OF TRANSPORT

There are two mechanisms by which chemicals can be transported through soil liners: advection and diffusion. Freeze and Cherry (1979) define advection as "the process by which solutes are transported by the bulk motion of the flowing groundwater." As waste liquid or leachate percolates downward through a soil liner, the flowing liquid carries chemicals dissolved in the liquid into and, ultimately, through the soil liner.

Diffusion is the movement of chemical constituents in response to a concentration gradient. If chemicals are present in the waste liquid or leachate at larger concentrations than in the soil liner and underlying subsoil, the chemicals will diffuse into and through the liner independently of the advective process.

Advection

Darcy's Law -- The rate at which advection takes place may be determined from Darcy's law (Freeze and Cherry, 1979), which can be written as follows:

$$q = k i A \quad 4.1$$

where q is the quantity of flow (Q) per unit time (t), k is the hydraulic conductivity, i is the hydraulic gradient, and A is the cross-sectional area of flow. The flux (v) is defined as the quantity of flow per unit area per unit time ($v = q/A$). The mass flux due to advection, J_a , is defined as the mass of a constituent passing through a unit area of the liner per unit time and is equal to the flux of water times the concentration of the constituent in the water, c , or:

$$J_a = \frac{c q}{A} = c k i \quad 4.2$$

The application of Darcy's law to a soil liner is illustrated with the aid of Figure 4.1. The compacted soil liner generally has a minimum thickness of 3 ft, and the disposal unit is typically designed so that the head of liquid above the liner is no more than 1 ft. A flexible membrane liner (FML) may or may not be placed directly on the clay liner, but for analyses of worst-case conditions, the FML can be assumed to be absent or ineffective.

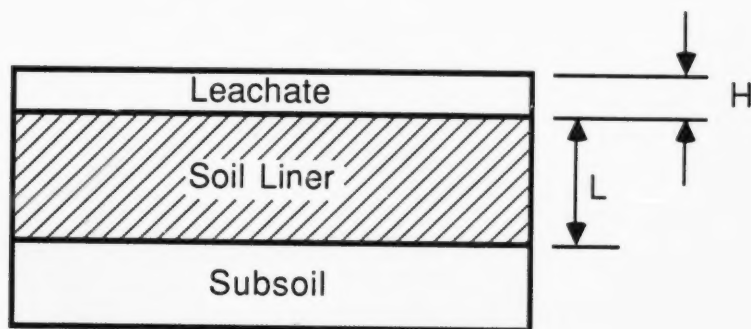


Figure 4.1 Compacted Soil Liner with Leachate.

The hydraulic gradient (i) that drives the flow of liquid through the soil liner is computed as follows:

$$i = \frac{H + L + P}{L} \quad 4.3$$

where P is the suction head in the underlying subsoil. If the suction head is zero, then:

$$i = \frac{H + L}{L} \quad 4.4$$

For the typical design case in which $H = 1$ ft and $L = 3$ ft, the hydraulic gradient from Eq. 4.2 is equal to 1.33. If the suction head in the subsoil is significantly greater than zero, then the hydraulic gradient will be greater than 1.33. For example, if the suction head is 0.5 bars (1 bar = 33 ft of water head), $H = 1$ ft, and $L = 3$ ft, then the hydraulic gradient (Eq. 4.3) is 6.8.

Time of Travel -- Equation 4.2 gives the mass flux of a constituent into the liner but says nothing about how long it will take for the constituent to pass through the liner. The situation shown in Figure 4.2 illustrates an idealized liner with a constituent present in the leachate at a constant concentration c_0 . For purely advective transport and no mechanical dispersion, the pattern shown in Figure 4.2 is expected to develop. Initially, leachate enters the liner and begins to soak the initially unsaturated soil liner. With time, the constituent moves downward until it eventually reaches the bottom of the liner. For these assumptions, the concentration (c) of the constituent in the liquid emerging from the bottom of the liner can be plotted vs. time, and the result would be as shown in Figure 4.3. Theoretically, there would be a sudden change in the concentration of the constituent in the effluent liquid from zero to c_0 . The time at which this sudden change in concentration occurs is termed the "time of travel," or TOT.

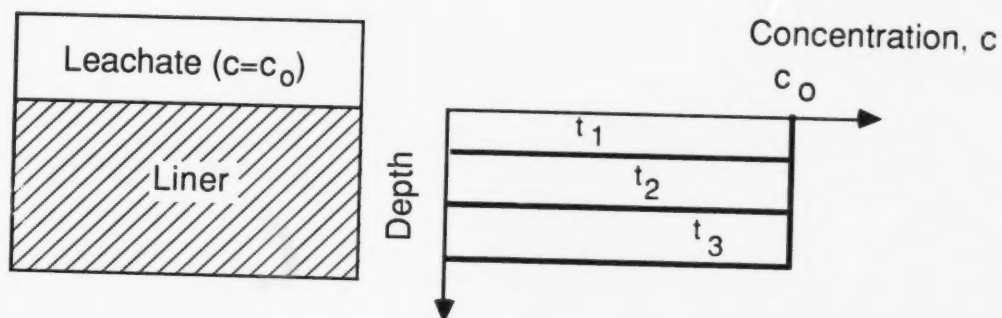


Figure 4.2 Idealized Leachate Movement through a Soil Liner

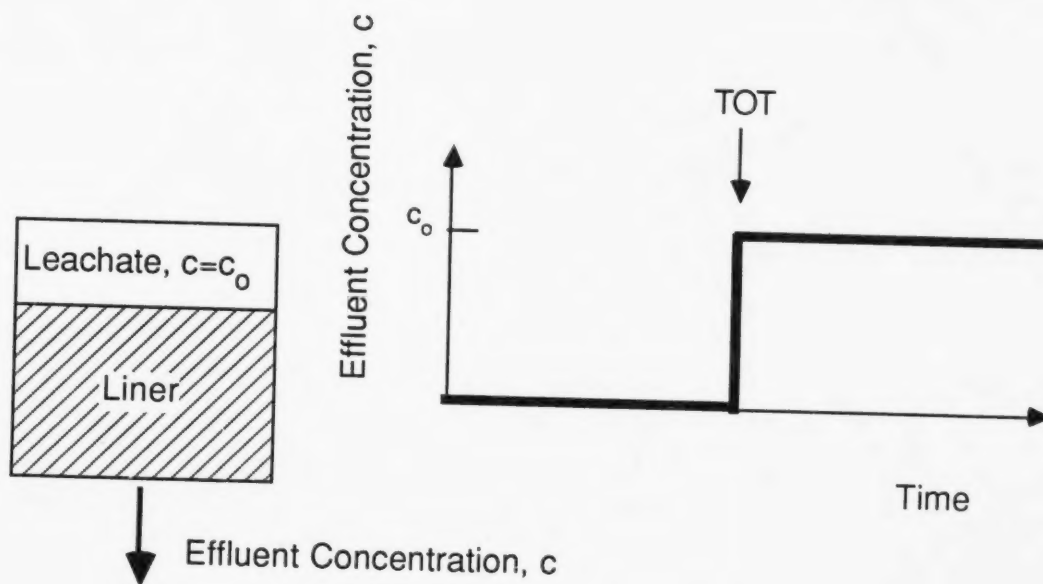


Figure 4.3 Time of Travel (TOT) of Constituent through a Soil Liner

The time of travel can be calculated for saturated soils based on the velocity of seepage, v_s , of the flowing water. The seepage velocity is defined as the average velocity of the water along the path of flow and is computed as follows:

$$v_s = \frac{k i}{n_e} \quad 4.5$$

where n_e is the "effective porosity," i.e., the volume of the pore space conducting flow divided by the total volume of the soil material. For unsaturated soil, the hydraulic gradient and hydraulic conductivity vary as the water content of the soil changes. Computer programs such as SOILINER (EPA, 1984) are typically used to analyze time of travel through unsaturated soil.

Mechanical Dispersion -- In reality, advective transport of a constituent through a soil liner is more complex than indicated by the preceding discussion. The leachate mixes with soil water, and this mixing (termed "mechanical dispersion") tends to spread out the leachate front and the appearance of the constituent in effluent from the liner (Figure 4.4).

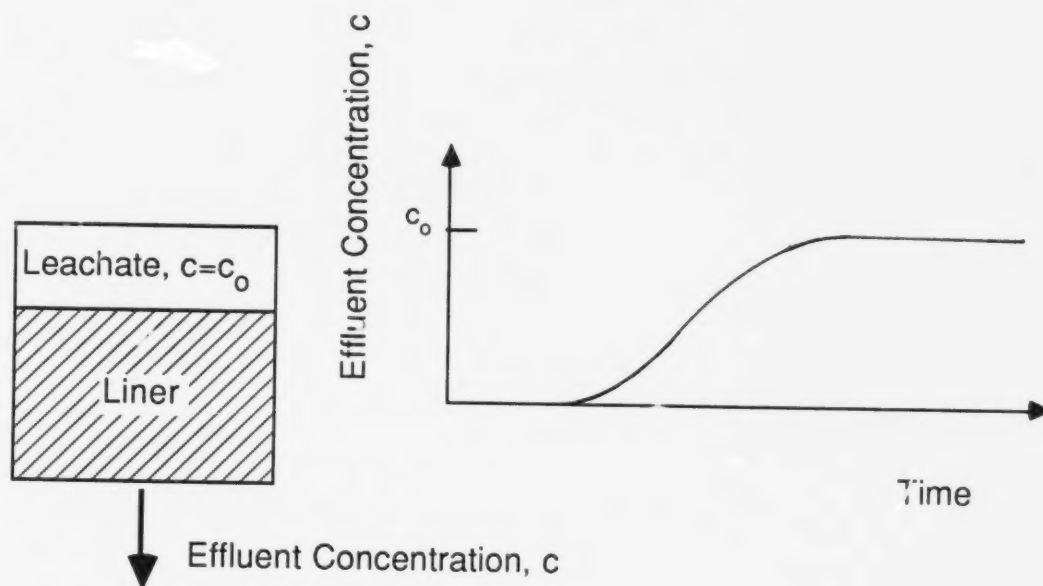


Figure 4.4 Breakthrough of Constituent with Mechanical Dispersion

Retardation of Solutes -- Some solutes in waste liquids and leachates are sorbed by soil through processes such as ion exchange and precipitation (Freeze and Cherry, 1979). In effect, some solutes migrate through soil more slowly than the transporting water. Indeed, the time of travel of different constituents may be quite different, depending upon the extent to which the constituent is sorbed by the soil or upon geochemical reactions, e.g., precipitation. Usually, time of travel calculations are based upon the most mobile constituent, i.e., the constituent that is least retarded by the soil. A conservative assumption is that the most mobile constituent will not be significantly retarded or otherwise slowed as it is transported by water through the soil liner.

Diffusion

Constituents in waste liquids and leachates can also pass through a soil liner via molecular diffusion. The process is illustrated in Figure 4.5, in which it is assumed that the concentration of a constituent in the liquid above the soil liner is c_0 and the initial concentration in both the liner and subsoil is zero. Over time, the constituent diffuses into, and ultimately through, the liner.

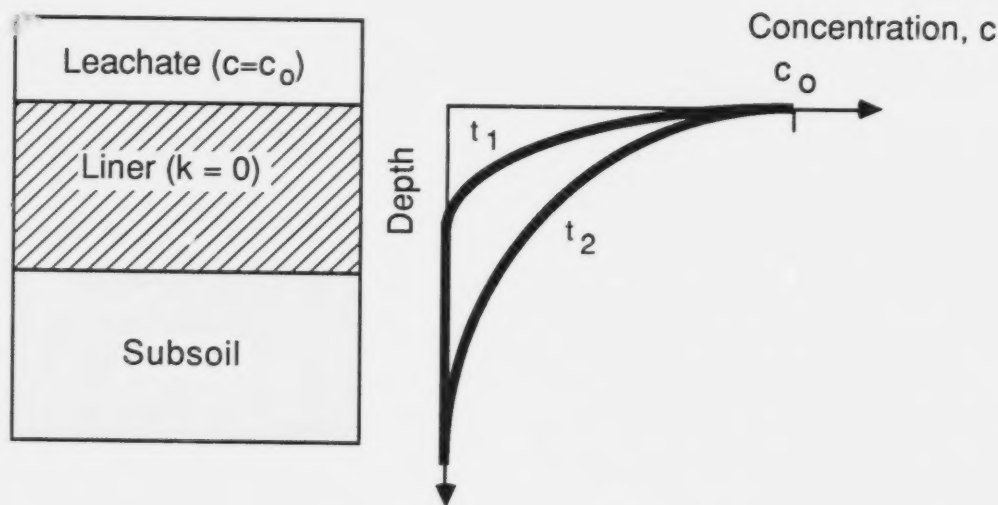


Figure 4.5 Movement of a Constituent through a Soil Liner by Molecular Diffusion

In soils of high hydraulic conductivity, molecular diffusion is thought to be a relatively unimportant mechanism of solute transport (because advection dominates diffusion), but in soils with low advective velocities of transport (soils having low hydraulic conductivities and/or low hydraulic gradients), molecular diffusion can be an important, if not dominant, mechanism of transport. The importance of diffusion for transport of solutes through clay soils is discussed in more detail later in this section.

ISSUES PERTAINING TO ADVECTIVE TRANSPORT

Validity of Darcy's Law for Flow at Low Gradients in Clay Soils

Although Darcy's law is an empirical equation, it has been successfully applied to analysis of hydraulic flow in sands and granular materials. It is a general belief that Darcy's law is valid for fine-grained soils, too (Olson and Daniel, 1981). However, some researchers (Lutz and Kemper, 1959; Hansbo, 1960; Li, 1963; and Miller and Low, 1963) have reported that the hydraulic flow rate through fine-grained soils did not obey Darcy's law, especially at low gradients. The experimental results generally followed the trend shown in Fig 4.6. If Darcy's law is valid, a plot of flux (v) versus hydraulic gradient (i) should be a straight line (as shown in Fig. 4.6a) with a slope that is equal to the hydraulic conductivity (k). However, some experiments have suggested that with a hydraulic gradient that is less than the "threshold gradient," there is no flow (Fig. 4.6b).

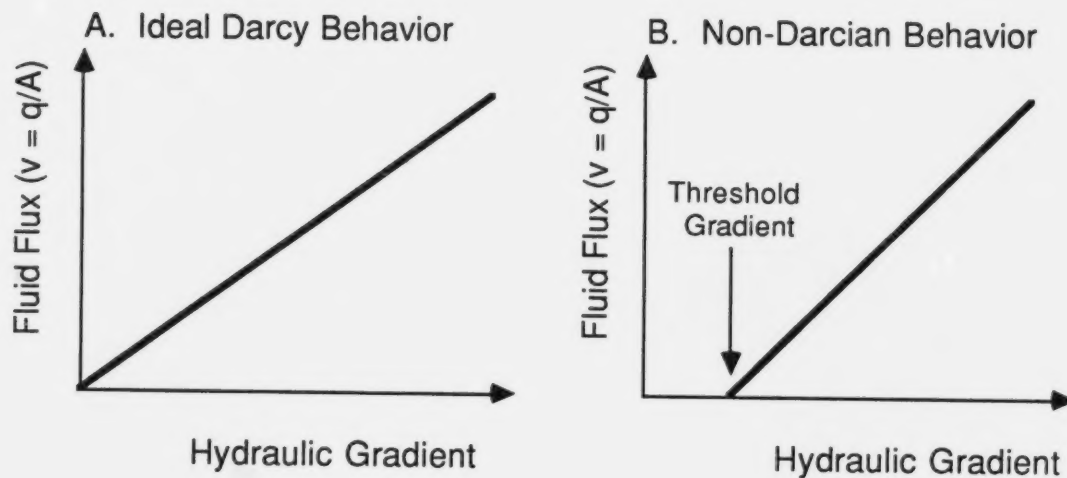


Figure 4.6 (A) Darcian and (B) Non-Darcian Flow through Soil

According to Olsen (1965), some of the findings indicating the existence of a threshold gradient were due to the use of contaminated tubes as a volumetric measurement device in the experiments, such as Hansbo (1960) and part of Miller and Low (1963). But the rest of the findings could not be attributed to experimental errors.

Miller and Low (1963) employed Li-clay and Na-clay pastes in hydraulic permeation tests at three temperatures. Their experimental results showed that under

the threshold gradient of 0 to 70, there was no flow through the clay paste. Miller and Low explained the threshold gradient on the hypothesis of a quasi-crystalline water structure near the surfaces of clay particles that developed in the clay-water system as a result of water-surface interaction. The water adsorbed in the double layer was assumed to be quasi-crystalline. At low gradients, it was postulated that the soil water was too viscous to permit measurable flow.

Lutz and Kemper (1959) investigated the effect of the thickness of diffuse double layer on the permeability of two bentonites, halloysite, and Bladen clay. Their results showed that permeability of the Na-bentonite increased as the hydraulic gradient was increased. Lutz and Kemper attributed this phenomenon to a breakdown of the quasi-crystalline adsorbed water at high gradient. However, Olsen (1966) criticized their experiments on the basis of lack of confinement and use of large gradients, which were favorable for seepage-induced fabric changes.

Mitchell and Younger (1967) permeated two fine-grained soils and monitored the pore water pressure within specimens during permeation. The results from one soil, kaolinite, showed a linear relationship between fluid flux and gradient. Another soil used in Mitchell and Younger's study was a silty clay in which hydraulic flow was not in accord with Darcy's law at gradients between zero and 16. Although the diagram of flow rate versus gradient indicated the existence of a threshold gradient of 6, measurable flow at very low rates actually did occur throughout the gradient range of zero to five. Another finding from the experiments on the silty clay was that the flow rate varied with time at certain gradients, and stayed constant at other gradients. Mitchell and Younger interpreted this instability in terms of particle migration and pore blocking effects. Further, the soil was subjected to successively decreasing gradients below 16. The data indicated greater flow rates in the condition of successively decreasing gradient than those in the tests of increasing gradient. Mitchell and Younger again regarded this behavior as the result of particle rearrangement.

In order to investigate the irregular flow phenomena, Mitchell and Younger developed a 1-ft-long permeameter to enable the measurement of pore water pressures at several point along the length of the specimen during permeation. The silty clay was directly compacted into the permeameter at different water contents and densities. It was observed that pore water pressures were unstable in early runs and that the distribution of pore water pressure was nonlinear. Also, the hydraulic conductivity of specimens was not homogeneous due to the application of gradient, which led to a relative densification (and lower conductivity) at the outflow end. From the experimental results, Mitchell and Younger concluded that particle migration took place in less dense specimens under the action of flowing water. A doubt on the existence of a threshold gradient was placed, and particle migration was considered as the cause of non-Darcian behavior in their experiments. Mitchell and Younger also argue that in the field the gradient was often not much larger than unity; thus the validity of experimental data based on large gradients should be questioned.

Law and Lee (1981) measured the hydraulic conductivity of a glacial till, which ranged between 10^{-7} and 10^{-8} cm/s. All their specimens showed some swelling which required a one-month waiting period before the calculated hydraulic conductivity was steady. The swelling resulted in more volume of water flowing into the specimens than water flowing out. The relation between flow rate and gradient was linear for all six till specimens with intercepts on the gradient axis at zero flow rate. The intercept was termed "initial gradient" and ranged from 0.09 to 2.93.

Silva et al. (1981) permeated fine-grained marine sediments at gradients of zero to 30. The relationship of flow rate versus gradient was linear for all three specimens in 11 tests. However, the data indicated the existence of a threshold gradient in the specimens of lower void ratio and non-zero flow rates at a gradient of zero in the specimens of higher void ratio.

Olsen (1985) reviewed the work of Law and Lee (1981) and Silva et al. (1981) and suggested osmotic effects as the cause of non-zero intercepts in the experimental results. He attributed the source of osmosis to the external chemical gradient imposed at both ends of a specimen or the change of pore fluid chemistry. Olsen emphasized that when a chemical gradient is present, Darcy's law relates only to the component of liquid movement governed by hydraulic gradient.

Experimental errors could result in nonproportionality in plots of flow rate versus hydraulic gradient. The common errors may be summarized as follows:

1. Leakage, such as leakage through fittings, valves, and tubing. Undetected leakage may easily account for an apparent hydraulic conductivity of 1×10^{-8} cm/s (Mitchell and Younger, 1967) when the conductivity is in fact much less.
2. Improper measurement device for the flow rate. For instance, a contaminated capillary tube of 1 mm in inside diameter with an air bubble could induce a pressure drop of 1-2 cm across the bubble (Olsen, 1965).
3. Local swelling and consolidation of the soil specimen. The application of a hydraulic gradient can result in changed effective stresses and physical properties in a soil specimen. The importance of this effect varies with the magnitude of hydraulic gradient (Mitchell and Younger, 1967; Olson and Daniel, 1981).
4. Differences in the type and concentration of electrolyte between soil water and permeating water (Olsen, 1985, and Olson and Daniel, 1981).
5. Growth of microorganisms within specimens (Olson and Daniel, 1981 and Mitchell and Younger, 1967).
6. Entrapped air. Gas bubbles in a soil specimen can effectively reduce the void space that can be occupied by water and thus reduce hydraulic conductivity (Olson and Daniel, 1981).

There is no definite conclusion that can be drawn on the existence of threshold gradients. Numerous researchers reported that they did not observe a threshold gradient, while some did. The possible sources which have been proposed in the literature are: (1) an internal source of osmosis within a test specimen (Olsen, 1966), (2) a quasi-crystalline structure in water adjacent to clay particles (Miller and Low, 1963), and (3) experimental errors (Mitchell and Younger, 1967; and others).

Effective Porosity

The effective porosity, n_e , is defined here as the volume of pore space that is effective in conducting the flow of liquid divided by the total (bulk) volume of the soil.

The effective porosity is sometimes less than the total porosity of the porous medium because of the existence of non-conductive space, such as dead-end pores, isolated pores, gas-filled pores, and pores that are too small to conduct a significant amount of flow.

Relatively little is known about the effective porosity of compacted clay soils. Peyton et al. (1985) measured the effective porosity of a lacustrine clay by permeating a pulse of tracer through soil columns sampled from the field. Tritiated water and Rhodamine WT were added into the water as a tracer. The flow rates were between 0.04 and 0.11 mL/hr. The results showed that the effective porosity and total porosity were essentially the same.

Gibb et al. (1985) measured effective porosity of glass beads and Ottawa sand by conducting tests at flow rates ranging from 0.1 to 5 mL/min. Gibb et al. observed a decrease in hydraulic conductivity at flow rates of 3-5 mL/min. The observation was attributed to a decrease in effective porosity at higher flow rates (cause was unknown), which induced a rise in pressure to maintain a constant flow rate. However, the effective porosities measured in the study were equal to or greater than calculated total porosity, due to a combination of experimental errors, packing, and pore size distribution.

Horton et al. (1985) presented a method of determining the effective porosity of compacted soil materials. The determination of effective porosity was based on the total porosity and the pore size distribution of a compacted soil by using a graphical solution. Horton et al. measured the effective porosities of three soils by tracer studies and found effective porosities of 0.04, 0.04, and 0.08; the total porosities were 0.29, 0.40, and 0.46, respectively.

DIFFUSION IN SOIL

Theory

The process of diffusion is usually assumed to occur in accord with Fick's first and second laws. Fick's first law states that the diffusional mass flux is directly proportional to the spatial gradient in the concentration of solute. For diffusion in free solutions, Fick's first law may be written:

$$J_d = -D \frac{\partial c}{\partial x} \quad 4.6$$

where J_d is the diffusional mass flux, c is the concentration of a solute, x is the direction in which the diffusion is occurring, and D is the diffusion coefficient in the medium in which the diffusion occurs. In free solution, D is equal to the free-solution diffusion coefficient, D_0 , which, for a specific compound, can be looked up in chemical handbooks or computed (Shackelford, 1988).

For porous materials, the diffusion coefficient is less than the free-solution diffusion coefficient because (1) diffusion takes place only in the pores of the material and not in the solid phase, and (2) the diffusional paths around the solids particles in the porous material are more tortuous than the unobstructed paths encountered in free solutions. The effective diffusion coefficient, D^* , in soils may be calculated as follows for solutes that do not react with the porous material:

$$D^* = \tau D_0$$

4.7

where τ is a "tortuosity factor" that accounts for the tortuous nature of the diffusional path around soil particles and n is the porosity of the soil (Shackelford, 1988). The experimental values of tortuosity factor that have been reported in the literature are 0.7 for granular soil (Bear, 1972), 0.35 for clayey till (Rowe et al., 1985), and a range from 0.03 to 0.53 for various media (Cunningham and Williams, 1980, p. 223).

The tortuosity factor is a geometric property of the porous medium and should be independent of solute species. However, different species may migrate along different paths, as noted by Rowe et al. (1985), resulting in a different tortuosity factor for different species.

Fick's second law describes the transient transport of solute by the following partial differential equation (Shackelford, 1988):

$$\frac{\partial c}{\partial t} = D^* \frac{\partial^2 c}{\partial x^2}$$

4.8

Solutions for Eq. 4.8 with appropriate initial and boundary conditions could be obtained by the technique of Laplace transform or by numerical methods. The solution yields the concentration of solute with respect to time and space. Analytical solutions can be found in Crank (1975) and elsewhere.

Data

The observation by Goodall and Quigley (1977) for the Confederation Road sanitary landfill site near Sarnia, Ontario, Canada, was probably the first well documented case of diffusional transport of pollutants in soil. The concentration profiles of calcium, magnesium, and sodium underneath the landfill were measured in the pore water squeezed out of soil samples. The migration of pollutants had proceeded 30 cm downward for 7 years, while the seepage front based on hydraulic conductivity was estimated to have advanced only 4 cm. The advance could be explained by one-dimensional Fick's law with an effective diffusional coefficient of $1.5 \times 10^{-6} \text{ cm}^2/\text{sec}$. Goodall and Quigley concluded that diffusion was the dominant mechanism of transport at the Confederation Road Site.

Quigley et al. (1984) returned to the Confederation Road landfill site 15 years after operation. The pollutants had migrated downward farther to a depth of 70-150 cm, as determined from the concentration profile of chloride. Diffusion was again found to be the dominant transport mechanism.

More field evidence of diffusion was provided by Johnson et al. (1986). They measured the chloride profile beneath a 5-year-old waste disposal site underlain by a 25-meter-thick natural clay deposit. The chloride migrated 83 cm downward, which was compatible with the diffusional advance with a diffusion coefficient of 2.0 to $6.0 \times 10^{-6} \text{ cm}^2/\text{sec}$, which was determined from their laboratory experiments. The results indicated that the influence of advection was negligible and that diffusion was the dominant mechanism of transport in the natural clay.

Laboratory experiments were conducted by Crooks and Quigley (1984) to measure the diffusion coefficients. Crooks and Quigley prepared in the laboratory a compacted,

silty clay similar to the silty clay at the Confederation Road landfill site. The laboratory diffusion coefficients of sodium and chloride were calculated from their migration profiles. After being corrected for temperature, the laboratory-determined diffusion coefficients agreed well with the field values.

Another laboratory diffusion experiment was performed by Gillham et al. (1984) for two nonreactive solutes (^{36}Cl and ^3H) and one reactive solute (^{85}Sr) in seven mixtures of bentonite and silica sand ranging from zero to 100% bentonite by weight. Their results were consistent with the Fickian diffusion equation.

A summary of experimentally measured effective diffusion coefficients for several inorganic ions is provided in Shackelford (1988). The typical range of effective diffusion coefficients for anions diffusing in soil is from 1.0×10^{-6} to 1.5×10^{-5} cm^2/sec .

ADVECTIVE-DISPERSIVE TRANSPORT OF SOLUTES IN SATURATED SOILS

Advective-Dispersive Transport Model

Based on the conservation of mass over a representative elementary volume, the transport in one dimension for a solute that does not react with soil can be described by the following partial differential equation:

$$\frac{\partial c}{\partial t} = D_d \frac{\partial^2 c}{\partial x^2} - v_s \frac{\partial c}{\partial x} \quad 4.9$$

where c is the concentration of solute, v_s is average velocity of fluid flowing in a porous medium, D_d is hydrodynamic dispersion coefficient, x is space coordinate, and t is time. The derivation of this partial differential equation was presented in Ogata (1970) and elsewhere.

Hydrodynamic dispersion was first observed by Slichter (1905), who performed field tracer tests to estimate groundwater velocity. It is now generally recognized that two processes contribute to hydrodynamic dispersion: (1) molecular diffusion, which is concentration-dependent, and (2) mechanical dispersion, which is advection-dependent. For one-dimensional flow, the hydrodynamic dispersion coefficient, D_d , can be written as the sum of these two components as follows:

$$D_d = a_L v_s + D^* \quad 4.10$$

where a_L is the longitudinal dispersivity and D^* is the effective diffusion coefficient of a solute diffusing in a porous medium. The first term on the right side of Eq. 4.10 represents mechanical dispersion while the second term takes into account molecular diffusion.

Mechanical dispersion is a mixing process due to velocity variations within a porous medium. On the microscopic scale of pore spaces, dispersion is attributed to 1) the velocity distributions within a pore channel due to the viscosity of water; 2) the velocity variations between flow channels due to the varying pore geometries; and 3) fluctuation of streamlines with respect to mean flow direction (Fried, 1975). On the macroscopic scale, further mixing occurs due to the heterogeneous nature of soil

deposits. Experimental data have shown that mechanical dispersion is a function of average fluid velocity, and quantitatively equal to the product of average fluid velocity and dispersivity, α_L , as shown in Eq. 4.10. Ranges of dispersivity of unconsolidated geological materials are presented in Gillham (1981). More data on dispersivity can be found in Anderson (1979, p. 126 - 127).

Adsorption and Retardation Processes

Adsorption Processes -- Adsorption can be treated as a chemical reaction in which mass transfer occurs by removing the solute from the liquid owing to the mutual attraction between the substance and the solid phase of the porous medium. For single-solute systems, the adsorbed mass of a specific ion is related to its concentration in free solution. The relationship is expressed in the form of an adsorption isotherm, which is a plot of the mass of a sorbed solute per mass of soil (S) versus the equilibrium solution concentration of the solute (c).

The adsorption isotherm at low concentrations is usually linear and represented by a straight line. The slope of this line is termed "distribution coefficient," K_d , in a plot of solid concentration versus liquid concentration at equilibrium. In the high concentration range, the adsorption isotherm is generally nonlinear. Linear and non-linear isotherms are sketched in Figure 4.7.

The adsorption of cations on the surface of clay particles is sometimes referred as "cation exchange" in the literature. Clay particles have negative surface charges due to isomorphous substitution, broken bonds, and replacement of hydrogen in exposed hydroxyls (Grim, 1968). In general, cation exchange is regarded as a reversible process governed by thermodynamic equilibrium. Cations of higher valence generally are more strongly attracted to clay particles. Ions of smaller hydrated radii are more readily adsorbed than ions with larger hydrated radii. The "selectivity coefficient" relationship has been proposed to describe ion-exchange equilibria among multiple cations. The selectivity coefficients have been treated as mass-law constants, although these coefficients are not thermodynamically well defined (Stumm and Morgan, 1981).

The adsorption isotherm is measured with a batch-adsorption test. In this test, the soil is mixed with solution containing one or more solutes of interest at a pre-determined ratio of liquid and soil. The soil-liquid mixture is mixed until equilibrium is achieved. Then, the solid and liquid phases are separated by centrifugation. The concentration (c) of the solute of interest is measured. Based on the known initial concentration and the final concentration of the solute in solution, the amount of solute sorbed by the soil is calculated. More details on the batch adsorption test are given by Griffin et al. (1986).

Equations for Adsorption Isotherm -- Many adsorption isotherm equations have been used to fit the sorbed and equilibrium concentrations resulting from batch equilibrium tests. The three most common equations are the linear, Freundlich, and Langmuir relations. These three isotherm equations have been used to fit a wide variety of adsorption data (Bohn et al., 1979).

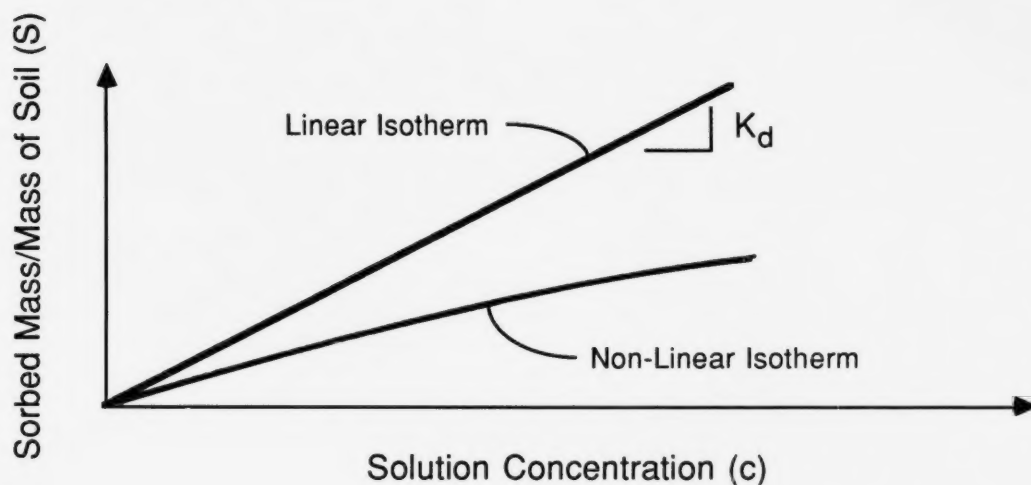


Figure 4.7 Adsorption Isotherms

The equation for a linear isotherm is:

$$S = K_d c \quad 4.11$$

where S is the mass of solute sorbed by a unit mass of soil, K_d is a partitioning coefficient termed the "distribution coefficient," and c is the equilibrium concentration of solute in solution.

The Freundlich isotherm is given by:

$$S = K_f c^N \quad 4.12$$

and the Langmuir isotherm by:

$$S = \frac{K_L M c}{1 + K_L c} \quad 4.13$$

where K_f and N in Freundlich isotherm and K_L and M in Langmuir isotherm are the adjustable parameters to best-fit the experimental data. The values of K_f and N are obtained from the plot of $\log c$ vs. $\log S$. The best-fit for the experimental data can be determined on the basis of linear regression analysis. The slope of this line is equal to the value of N , and the y-intercept is equal to K_f . The values of K_L and M are determined by a similar approach from the plot of c versus c/S .

For isotherms of the form shown in Figure 4.7, the retardation factor (R_d), which is equal to the velocity of the moving fluid divided by the velocity of the solute, may be written as:

$$R_d = 1 + \frac{\rho_b}{n} K_d \quad (\text{Linear}) \quad 4.14$$

$$R_d = 1 + \frac{\rho_b}{n} K_f c^{N-1} \quad (\text{Freundlich}) \quad 4.15$$

$$R_d = 1 + \frac{\rho_b}{n} \frac{K_{LM}}{1 + K_{LC}} \quad (\text{Langmuir}) \quad 4.16$$

which is based on the slope of the secant line from zero to the point on the isotherm at free-solution concentration, c . The symbol ρ_b indicates the dry bulk mass density of the soil and n denotes porosity.

Other adsorption equations in the literature include ion exchange isotherms for multi-ion adsorption (Charbeneau, 1981; Bolt, 1982); Brunauer-Emmett-Teller equation for multisite and multilayer adsorption (Bohn et al., 1979); Polanyi adsorption potential equation for heterogeneous adsorption sites for multi-solutes (Montgomery, 1985); Langmuir competitive adsorption model for multi-solutes (Tien, 1983); and ideal adsorbed solution model based on thermodynamic equivalence of the spreading pressures of multi-solutes (Weber, 1972).

Sources and Sinks -- In addition to adsorption processes, sources and sinks can affect the transport of solute through soils. Sources and sinks include precipitation-dissolution processes, chemical oxidation and reduction, biological consumption, and complex formation and chelation (Cherry et al., 1984 and Dunn, 1983). The processes vary with the chemical environment in the soil. The effects of sources and sinks are not easy to predict or control. Since sources and sinks are not the main focus of this study, no further investigation was executed.

Data

Many one-dimensional laboratory experiments have been conducted to determine the validity of the advection-dispersion equation. The experimental results have most frequently been presented in the form of a concentration history of the effluent from a column, or a breakthrough curve, which is a graph of relative concentration versus dimensionless time represented by the number of pore volumes of flow. Comparisons have been made between the breakthrough curves predicted by the model and from experimental results. Although Fried (1975) concluded from the study of then-available experimental results that, for practical purposes, the model is a good representation of the dispersion processes, discrepancies have been reported in the literature. The discrepancies between theoretical predictions and experimental results can be categorized with three aspects: (1) the dependence of the mechanical dispersion coefficient on average flow velocity, especially on a large scale where heterogeneity is expected; (2) the unsuccessful predictions of some column performances, for example, asymmetrical breakthrough curves and the influence of stagnant liquid; and (3) the limitation of the adsorption-isotherm approach. Since the first aspect is not the main focus of this study, only the latter two aspects will be reviewed in the following.

The unsuccessful predictions by the advection-dispersion model were noted by Scheidegger (1974), who concluded that nonexperimental, systematic discrepancies do occur; the discrepancies were attributed to the presence of dead-end pores and to solution-solid interface processes which were not accounted for in the spatial averaging process (Gillham and Cherry, 1982). In fine-grained materials where an anion was used as a tracer, the early appearance of the breakthrough curve has been attributed to anion exclusion (Thomas and Swoboda, 1970). In aggregated media, an extreme tailing of the breakthrough curve has been observed and attributed to the diffusion into and out of the intra-aggregate pores. An extreme tailing was also observed in partially saturated media, which was a result from diffusion into immobile zones of water (Biggar and Nielsen, 1960). Fried (1975) cited several experimental results which did not show symmetrical breakthrough curves, which suggested that dispersion may not be represented as a Fickian process, as suggested by Anderson (1984).

Discrepancies between the experimental results and the predictions based on batch isotherm tests for adsorbed species were reported by Rainwater (1985), Shackelford (1988), and Smith and Weber (1988). The use of the isotherm approach within the framework of the advection-dispersion equation inherently involves some uncertainties and limitations. The uncertainties exist because of the heterogeneous nature of geologic deposits, because of geochemical effects, and because of effects caused by the dynamics of the transport processes (Cherry et al., 1984). Cherry et al. argue that even if the aqueous system used in the determination of the distribution coefficient by the batch method has the same composition as the leachate, the condition in the fluid is different because of the distinct advancing zones of pollutants. Thus, the suitability of batch tests to obtain the partition coefficients is questionable.

It is generally recognized that local equilibrium is achieved when the rate of change of solute mass due to microscopic sorption process is much "faster" than that due to bulk flow process. James and Rubin (1979) showed that the transport equation with a linear-adsorption isotherm accurately predicted the migration of cations when the flow velocity was so slow that molecular diffusion was the dominant influence in the dispersion process. At higher velocities, when mechanical dispersion was dominant in the dispersion process, differences between measured and calculated breakthrough curves were observed. The assumption of local equilibrium, which is implied in the use of the partition coefficient based on batch isotherm tests, was examined by Valocchi (1985). Valocchi concluded that the distinction between equilibrium and kinetics is pragmatic rather than fundamental, and that the validity of the equilibrium assumption depends on a complex interplay between macroscopic transport properties (e.g., seepage velocity, hydro-dynamic dispersion, and time variation of mass input) and microscopic sorption properties (e.g., mass transfer coefficient, aggregate size, and distribution coefficient).

The problems noted in paragraphs above do not necessarily demonstrate that the advective-dispersive transport model is invalid or inappropriate; indeed, as mentioned earlier, Fried (1975) concluded that the model represents the dispersion process well. The data in the preceding paragraphs serve to illustrate that the processes involved in advective-dispersive transport are complex.

TRANSPORT OF SOLUTES IN UNSATURATED POROUS MEDIA

The validity of Darcy's law in unsaturated fine-grained soils has also been debated among researchers. But, Darcy's law is generally accepted as valid in unsaturated, clay soils for engineering purposes (Olson and Daniel, 1981).

A mathematic model for solute transport in unsaturated soil under unsteady conditions needs to account for the spatial and temporal variation in moisture content and the effect of the dispersion of solute. To describe the solute transport in unsaturated soils, two types of equations are necessary -- one is the continuity equation of water to describe the migration of water, and the other is the transport equation for solutes to account for the dispersion and adsorption of solutes under unsaturated conditions. The transport equation for non-adsorbed solutes in unsaturated soils bears the form:

$$\frac{\partial}{\partial t}(\theta c) = \frac{\partial}{\partial x} [\theta D_d \frac{\partial c}{\partial x}] - \frac{\partial}{\partial x} [v_s c] \quad 4.17$$

where θ is the volumetric water content and the rest of the variables are defined as before. The continuity of water for one-dimensional flow can be mathematically described as:

$$\frac{\partial \theta}{\partial t} + \frac{\partial v_x}{\partial x} = 0 \quad 4.18$$

where v_x is the discharge flux in the x direction. The discharge flux is a function of water content. When the migration of a solute is in the vertical direction, the flux can further be expressed in accord with Darcy's law as:

$$v_x = -k \frac{\partial h_p}{\partial x} + k \quad 4.19$$

where k is the hydraulic conductivity and h_p is the pressure head. Both pressure head and hydraulic conductivity of unsaturated soil are generally expressed as functions of water content, i.e., $h_p(q)$ and $k(q)$.

The relationship between water content and suction pressure is termed the moisture-characteristic curve in the literature. Equations for describing moisture-characteristic relationship are reviewed by van Genuchten and Nielsen (1985).

The hydraulic conductivities of unsaturated soils are generally expressed in terms of relative hydraulic conductivity, defined as k/k_{sat} , where k_{sat} is the hydraulic conductivity in the saturated condition. Equations for computing k/k_{sat} are also reviewed by van Genuchten and Nielsen (1985).

Equation 4.17 bears marked similarity to the transport equation for a saturated medium. However, for an unsaturated soil, the effective diffusion coefficient, the mechanical dispersion coefficient, and average fluid velocity are functions of volumetric water content. It has been shown that the effective diffusion coefficient in unsaturated soils can be orders of magnitude lower than in the same but saturated soil (see Shackelford, 1988, pp. 84-88). The decrease in the effective diffusion coefficient is mainly attributed to the reduction of the cross-sectional area available for diffusion and attributed to the increase in the effective path length through which diffusion occurs (i.e., a decrease in tortuosity factor). The mechanical dispersion coefficient of a soil increases as the soil desaturates (as indicated by Wilson and Gelhar, 1981), due to the longer travel paths and the existence of immobile regions of water.

For unsaturated porous media, the validity of Eq. 4.17 is questioned. de Smedt et al. (1986) studied tracer movement through an unsaturated sand column of 100 cm length and 15.4 cm diameter. The comparisons between breakthrough curves for

saturated and unsaturated soils indicated that the hydrodynamic dispersion was much larger for unsaturated sand. To explain this phenomenon, de Smedt et al. developed an alternative mathematical model to account for the influence of immobile phases of water. Analyses of results of the experiments showed that on the average 64% of the water in the sand column could be considered mobile and 36% immobile. de Smedt et al. attributed the most of dispersion to the transfer of solute between the mobile water phase and the immobile water phase.

The analysis of solute movement in unsaturated soil is an active area of research. New mathematical approaches are likely to evolve in the next few years.

SECTION 5

EXPERIMENTAL PROGRAM AND PROCEDURES

SOILS

Two clay soils were used in this test program: kaolinite and Lufkin clay. Kaolinite is a commercially-processed material (Georgia Kaolin Company, Elizabeth, New Jersey) consisting of practically pure kaolinite. This material was selected because it has been used for earlier studies, is readily available to all researchers, has a hydraulic conductivity after compaction near the upper limit of that allowed by EPA (1×10^{-7} cm/s), and has a low cation exchange capacity. Lufkin clay was selected because it has been used for earlier studies (Brown and Anderson, 1983; and others), is a naturally-occurring soil, has a hydraulic conductivity near the low end of the range typically observed for clay soils, and has a high cation exchange capacity. Data on the soils are given in Table 5.1.

LIQUIDS AND TRACERS

The tracers chosen for this study were zinc chloride and/or potassium bromide at a concentration of 0.01N. The tracers were added to 0.01N CaSO_4 prepared from distilled water. The pH of the tracer solution was adjusted, as necessary, to maintain a constant pH of 5.5 by addition of sodium hydroxide.

Bromide and chloride are nonreactive (not sorbed by soil). Bromide was chosen as a primary tracer because of its scarcity in nature. Chloride was used as a secondary tracer. Zinc and potassium are cationic tracers that are sorbed by most clay soils. Potassium and zinc were selected because they are relatively mobile in soils, compared to other metals. Potassium was expected to be more mobile than zinc. The concentrations of tracers in column tests were arbitrarily chosen to be 0.01N for all the tracer tests, except one series of tests at a concentration of 0.001N on kaolinite under a gradient of 5.

CHEMICAL ANALYSES

Tracers were analyzed with ion chromatography and flame atomic absorption. Approximately 10 to 20 mL of effluent sample was available for analysis. The samples were collected and stored in sealed glass containers, typically for 1 to 2 mo, prior to analysis.

Samples to be analyzed for cationic tracers were handled as follows. One mL of the sample was mixed with 20 to 100 mL (depending on the concentration of the cationic tracer in the effluent sample) of 0.15% nitric acid. The diluted solution was analyzed for concentration of cationic tracers with a Model 303 Atomic Absorption Spectrophotometer manufactured by Perkin-Elmer. The concentrations of standard solutions ranged 0-3 mg/l for zinc and 0-4 mg/l for potassium. These standard

Table 5.1 Properties of Soils

Property Method	Kaolinite	Lufkin Clay
Natural Water Content, % (ASTM D-2216)	—	23
Clay minerals (X-ray diffraction)	Kaolinite	Smectite
Color	White	Grey
Specific Gravity (ASTM D-854)	2.64	2.69
Percent Finer than No. 200 Sieve (ASTM D-422)	100	82
Unified Soil Classification (ASTM D-2487)	MH	CH
Compaction Data (ASTM D-698, Method A)		
Optimum Water Content (%)	32	20
Maximum dry unit weight (pcf)	83	102
Cation Exchange Capacity (CEC) meq/100g dry soil (Rhoades, 1982)	5	25
Exchangeable Cations meq/100g dry soil (Thomas, 1982)		
Na	3.8	6.4
K	0.8	2.7
Ca	1.0	19.1
Mg	<0.1	<0.1
Zn	<0.1	<0.1
Background Ion Concentration mg/l on saturation extracts (Thomas, 1982)		
Cl	7.1	179.0
Br	4.7	5.6
K	3.2	4.7
Zn	<0.2	<0.1
Soil pH (McLean, 1982)	3.7	6.9

solutions were prepared by the use of an analytical balance or from 1000 ppm stock solutions sealed by major manufacturers such as Fisher Scientific or VWR Co. The samples were diluted in various ratios down to the concentration range of standard solutions. The solution for dilution purposes was 0.15% nitric acid to prevent precipitation of tracers, plating of cationic tracers on container surface, and biological consumption of tracers. The spectrophotometer was calibrated by the standard solutions before and after the samples were analyzed. The analysis of one sample required an average 1 to 2 minutes.

The analyses for anionic tracers, chloride and bromide, were conducted with a Model 10 Ion Chromatograph manufactured by Dionex Co. The analysis procedures used in this study followed Test Method 300.0 in EPA Methods for Chemical Analysis of Water and Wastes. Although this method does not specifically list bromide, the method is generally applicable to all halides. Standard solutions of chloride and bromide were prepared from sodium chloride and sodium bromide by the use of an analytical balance. The range of concentration for chloride was 3-20 mg/l and 8-40 mg/l for bromide. Analyzing one sample took 20-30 minutes, which was the time for the sulfate in the sample to appear on the strip chart recorder. Chloride took 5 minutes, and bromide 12 minutes to show the peak in a strip chart. About 10 samples could be analyzed a day.

BATCH ADSORPTION TESTS

Variables

Several factors can influence the results of a batch adsorption test. The solution pH, mixing method, soil-to-solution ratio, and time to reach equilibrium are especially important variables. In order to apply the results from the batch test to interpret the results of column tests, the selected values for these factors need to be representative of those in the column tests. The soil-to-solution ratio by weight was 1:4. This ratio was obtained based on the volume of the solution passing through the soil column and the amount of soil compacted in the soil column. Up to 10 pore volumes of flow, or 4500 grams of water, passed through the kaolinite soil columns, which had 1300 grams (dry weight) of soil in it. This resulted in the ratio of 1:4, which is about the highest practical soil-to-solution ratio to use in batch tests.

A rotary tumble-mixer was used to mix soil and solution for 24 hours as suggested in ASTM method ES-10. The rotary motion allowed the liquid to flow from one to the other end of the container. This was to assure the free contact between soil particles and solution.

The pH values of added solutions were adjusted to between 6 to 8 which was the pH range in tracer tests. The ambient temperature was about $22 \pm 1^\circ \text{C}$.

Procedures

Five grams of soil were weighed in a centrifuge tube of 50 ml capacity. Then 20 ml of solution containing ions of interest were added to the tube. The concentrations of ions in the solution was so arranged that the equilibrium concentrations after 24 hours in liquid phase would distribute from zero to 0.01N. The series of initial concentration in the solution was 0.001N, 0.0035N, 0.005N, 0.0075N, 0.01N, 0.015N, and 0.02N.

The mixture of soil and solution was then mixed by rotary tumbler for 24-48 hours in the centrifuge tube. The solution was separated by centrifugation at 2000 rpm for 30 minutes. The supernatant was decanted and analyzed for the equilibrium concentration. The difference in concentrations was used to calculate the mass adsorbed by the soil. The relation between the adsorbed mass and the equilibrium concentration is generally expressed as an adsorption isotherm.

DIFFUSION TESTS

Equipment

A schematic representation of the fixed-wall diffusion cell used in this study is presented as Figure 5.1. The diffusion cell consists of a 4-inch-diameter, clear acrylic reservoir connected to the top of a 4-inch-diameter, Grade 304 stainless-steel compaction mold containing the compacted soil. An O-ring was stretched to fit around the top of the compaction mold to act as a seal between the reservoir and the mold. The reservoir and mold were compressed against each other, through the O-ring, by attaching and "bolting" together top and bottom plates with 3/8-inch-diameter, fully threaded stainless-steel rods. The top and bottom plates were taken from existing fixed-wall permeability equipment and were made of either aluminum or clear acrylic (plastic). Seals between the top plate and the reservoir were achieved with either an O-ring (for the aluminum top plate) or a rubber gasket (for the plastic top plate), whereas the seal between the bottom plate and the compaction mold was achieved with an O-ring in all cases.

A sampling port was installed about one inch above the bottom of the reservoir. A 1/8-inch-outside-diameter clear Teflon tube approximately 10 to 18 inches long with an attached two-way valve was fitted to the sample port. The sample port was used to fill and drain the diffusion system as well as to draw samples from the reservoir during the diffusion test. The tube was not drained prior to collecting a new sample. However, the volume of liquid in the tube was < 0.5 mL, which is far less than the sample volume of 25 to 50 mL. Thus, the water contained in the tube was of insignificant volume.

Two other holes (one in the bottom cap and one in the top cap), allowing flow into or out of the diffusion cell, existed. Depending on the soaking procedure, the hole in the bottom cap was either sealed during the soaking procedure or it was attached with a 1/8-inch-diameter clear Teflon tube to a T-section fitted to the threaded hole in the top cap. In all cases, the threaded hole in the bottom cap was sealed during the diffusion test period. Again, depending on the soaking procedure, the hole in the top cap was either fitted with a T-section and a two-way valve or just a two-way valve. The T-section was removed during the diffusion test.

The two-way valve attached to the top cap was connected to a 50-ml, pinch-cock buret by a 1/4-inch (I.D.) by 3/8-inch (O.D.) clear, flexible PVC tubing as shown in Figure 5.2. The buret was used to provide volume change readings during both soaking and diffusion periods. The volume of the compaction molds was either the standard 1/30 ft³ of ASTM D-698 or half that size (1/60 ft³).

Three different size reservoirs corresponding to lengths of 3, 3-7/8, and 5-1/4 inches were used in the study. Due to the 3/8-inch overlap at the connection between the reservoir and the compaction mold, the volumes of the three reservoirs were approximately 540, 720, and 1000 milliliters, respectively. However, the total

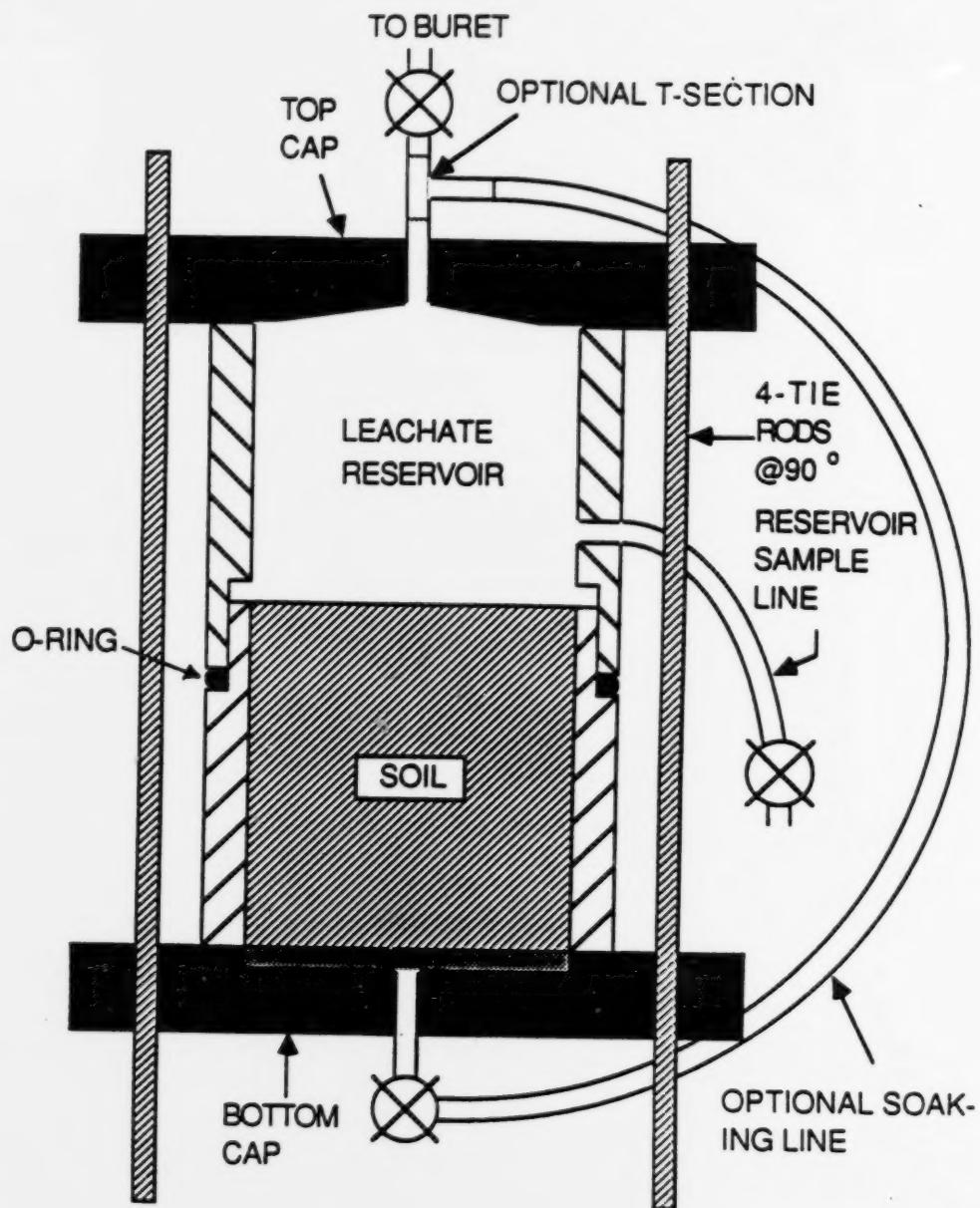


Figure 5.1 Schematic Drawing of Diffusion Cell

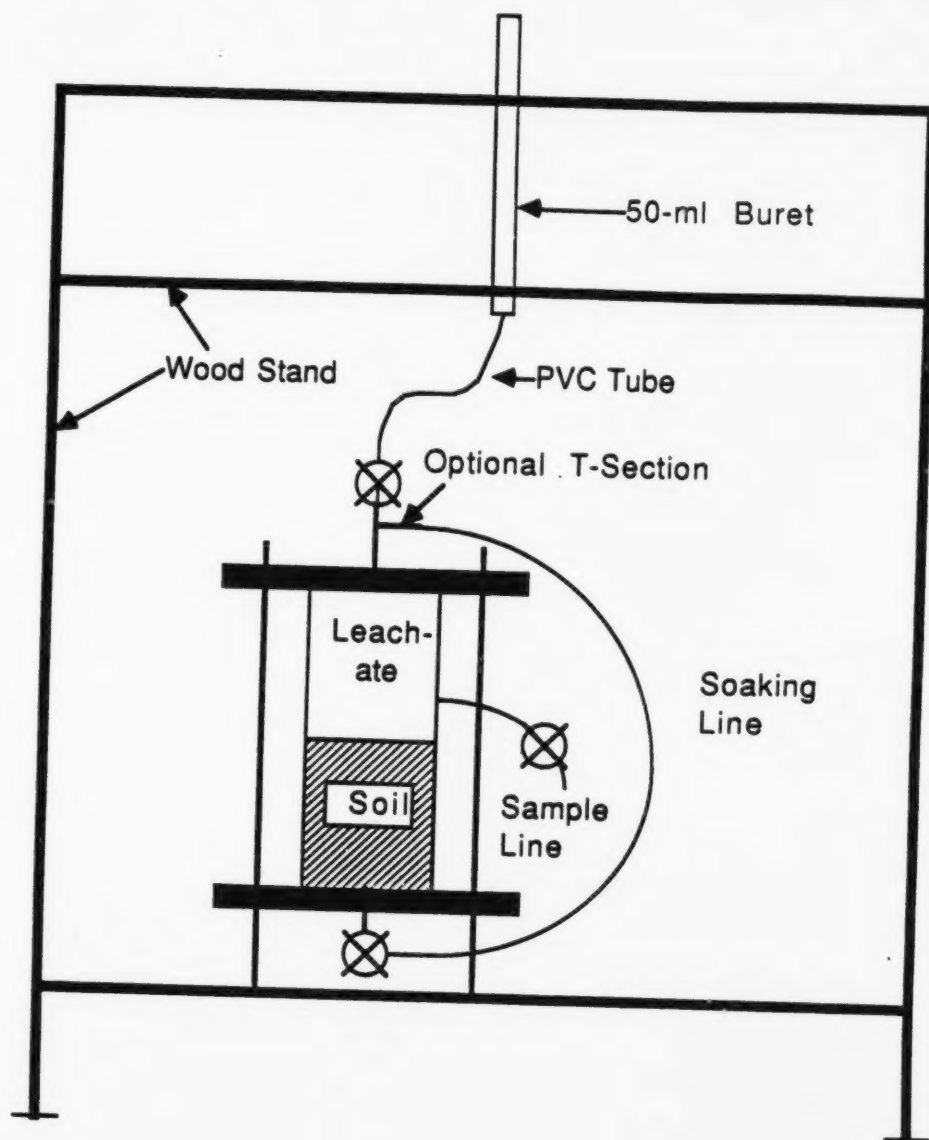


Figure 5.2 Schematic Drawing of Diffusion System

volumes of the soaking solution and leachate used in each diffusion test were greater than the reservoir volumes alone due to the capacities of the top caps, PVC tube, and the burets. The total volumes also varied from test to test due to the use of different top caps and lengths of PVC tube. Only the two smaller reservoirs were used during the diffusion test period.

Procedures

The procedures for performing the diffusion tests may be divided into five parts: (1) a sample preparation stage, (2) a soil-soaking stage, (3) a diffusion stage, (4) a "break-down" stage, and (5) a chemical analysis stage. The first four of these stages is discussed in detail in the following subsections. Procedures for chemical analysis are described in a later section.

Preparation of Soils -- The clay samples for the diffusion tests were prepared with the intent to make them as uniform as possible.

The Lufkin clay was air-dried and pulverized before preparation. The kaolinite was already dry and pulverized in its natural state. The Lufkin clay was broken by hand into relatively small clods (<2 inches) and the clods were air-dried for one week. The moisture content of the air-dried Lufkin clay was approximately five percent. After air-drying, the clods were passed through a mechanical pulverizer to reduce the clod size and then sieved through a No. 10 (2 mm) sieve size. The material passing the sieve was collected and the material retained on the sieve was re-pulverized. This procedure was repeated until a sufficient amount of material had been collected.

Test specimens of clay were prepared by mixing the air-dried soil with "standard" water (0.01 N CaSO_4) until the desired moisture content was obtained. The soil and water were mixed in a rotating mechanical mixer. The water was applied to the soil by spraying in a fine mist with a plastic spray bottle. The mixed soil was then placed into double plastic bags which were sealed and subsequently placed in a moist room for one week to allow for uniform hydration of the soil. After the hydration period, the soil was removed from the plastic bags and compacted into the diffusion cells.

The kaolinite and Lufkin clay were compacted with standard Proctor procedures, except for soils that were compacted into molds with half the normal height. The same compactive energy (12,375 ft-lb/ft³) was used for the half molds.

Soaking Stage -- Several modifications were made to the soaking procedure during the course of the study. The modifications were made primarily to save the amount of time required to soak the samples. Since the modifications evolved as the testing program progressed, the description of the soaking procedure will be made in chronological order.

The kaolinite was the first soil tested. The soaking procedure was as follows:

1. The soil was compacted into standard molds (1/30 ft³) and set-up in the diffusion cell.
2. The soaking solution (0.01N CaSO_4) was introduced into the system until the volume reading in the buret was about zero.
3. The soil was allowed to soak from both the top and the bottom, and volume readings were recorded periodically.

4. The soaking solution was withdrawn from the system after a soaking period ranging from 77 to 81 days, and the cell was disassembled so that the soil, which had swelled could be trimmed flush with the top of the mold.
5. After trimming, the cell was re-assembled and the soaking solution re-introduced into the system to establish equilibrium again.
6. After an additional soaking period of about 50 days, the reservoirs were changed from the largest reservoir (5-1/4-inch length) to the smallest reservoir (3-inch length); this required withdrawing the soaking solution, disassembling the cell, changing the reservoirs, re-assembling the cell, and re-introducing the soaking solution; equilibrium was re-established about four weeks after the change of reservoirs.

An air pressure/vacuum system consisting of a panel board and an acrylic accumulator connected by flexible Teflon tube was used to fill and withdraw the soaking solution from the reservoir. Details of this equipment are given by Foreman (1984).

A separate buret filled with soaking solution was set-up in order to account for evaporation during the soaking period. The volume readings for the separate buret were recorded at the same time as those for the soil samples.

A substantial amount of air accumulated in the reservoir beneath the top cap after the first day or two of soaking. Attempts were made to flush the air out of the system so that the subsequent volume readings would be accurate. Since the purpose of recording the volume readings was to establish when the system was in equilibrium, the total volume of soaking solution absorbed by the soil was considered to be relatively unimportant. Usually, most of the air could be removed with little effort within a reasonable amount of time (one to two hours).

Air bubbles also became trapped in the flow line connecting the bottom of the cell to the top. Due to the small diameter of this line, it was much more difficult, if not impossible, to keep air from clogging these lines. As a result, the soaking procedure was modified for subsequent tests; the soils were first soaked for a few days with the top open to the atmosphere.

The decision to change the reservoir size (step 6) was based on a desire to ensure that a significant percentage (>10 percent) of the initial mass of the constituents in the leachate would diffuse into the soil during the diffusion test period. In general, the smaller the reservoir, the greater the percentage decrease in initial solute concentration, all other factors being constant. Therefore, it was decided that the relatively large, 5-1/4-inch length (1000-ml) reservoir be replaced with either the 3-inch (540-ml) or 3-7/8-inch length (720-ml) reservoirs. In this case, the 3-inch length (720-ml) reservoirs were used. The change was made during the soaking period, rather than between the soaking and diffusion periods, to minimize the chances of significant mass flow occurring at the beginning of the diffusion period due to a disturbance to the system.

The soaking procedure used for kaolinite samples was changed completely for the Lufkin clay samples in an attempt to reduce the total soaking time. The soaking procedure for the Lufkin clay samples included the following steps:

1. The soil was compacted into half-sized molds ($1/60 \text{ ft}^3$) instead of the standard molds used for the kaolinite samples.
2. The compacted samples were then totally immersed in 0.01 N CaSO_4 solution.
3. After about two weeks of immersion, the samples were removed, the ends were trimmed flush with the mold, and the samples were re-inserted into the soaking solution.
4. After an additional 41 days of soaking, the samples were removed and set-up in the diffusion cells.
5. Soaking solution was introduced into the system and buret volume readings were recorded.

In each case, equilibrium between the reservoir and the soil was established within 15 days after the completion of the last step. Therefore, the total soaking period for the Lufkin clays was reduced to 70 days.

Diffusion Stage -- The diffusion stage was divided into two parts. First, the diffusion test was set up by introducing the simulated leachate into the reservoir. Second, concentrations of the ions of interest were monitored by periodic sampling of the leachate in the reservoir.

The diffusion tests were set up immediately after soaking to minimize drying of the top of the soil. Since the reservoirs which were to be used during the diffusion stage of the test were already in place at the end of the soaking stage, the diffusion cell did not have to be disassembled between the two stages. Therefore, disturbance to the system was minimized. The procedure for setting-up the diffusion test included the following steps:

1. The last buret volume reading from the soaking stage was recorded as was the evaporation buret reading.
2. The reservoir was partially drained by applying a vacuum through the sample port and a soaking-solution sample was taken; the pH, electrical conductivity, and temperature of the sample were recorded.
3. The pH of the diffusion liquid was adjusted to approximately that of the soaking solution by titrating the leachate with 0.1 M H_2SO_4 .
4. Samples of the diffusion liquid were taken for chemical analysis of the specified ions; also, the electrical conductivity and temperature of the liquid were measured and recorded.
5. The acrylic accumulator was filled with the leachate by applying a vacuum to the accumulator, and the weight of the filled accumulator was recorded.
6. The remainder of the soaking solution in the reservoir was drained by applying a vacuum through the sample port.
7. The reservoir was filled immediately after the soaking solution was withdrawn by connecting the bottom of the accumulator, filled with the

diffusion liquid to the valve at the sample port and applying a pressure (usually 20 to 30 psi) to the top of the accumulator; the buret volume and time were recorded after the diffusion system (reservoir, PVC tube, and buret) was filled.

8. The weight of the accumulator with the left-over leachate was recorded.
9. Two layers of 4-inch wide parafilm were stretched over the buret to minimize evaporation losses.

The volume of sulfuric acid (0.1M H_2SO_4) added to the leachate for adjustment of the pH (step 3) depended on the amount of liquid being titrated. However, the volume of the acid added for the pH adjustment usually was less than 0.5 ml and never was more than 2.0 ml.

The volume of the diffusion liquid initially introduced into the diffusion system was determined by taking the difference in the weights of the accumulator plus liquid measured both before (step 5) and after (step 8) the system had been filled. A density of 1 g/cc was assumed for the liquid when determining the volume.

The time required to fill the system with the diffusion liquid also varied but was never greater than four minutes. An elapsed time of four minutes is negligible with respect to the diffusion test periods, which ranged between one and three months.

Besides applying parafilm to the buret to minimize evaporation (step 9), a separate buret filled with diffusion liquid and covered with two layers of parafilm was assembled. The volume of the liquid in the buret was recorded each time a sample was taken from the reservoir and just before the diffusion test was disassembled. The volume change in the buret was negligible ($< 0.1 \text{ cm}^3$) throughout the entire diffusion test program, an indication that the parafilm acted as an effective barrier to evaporation.

After the diffusion test was set up, the concentration of solutes in the diffusion liquid was monitored periodically by withdrawing samples from the reservoir. The samples were analyzed for the specified ions to determine how the reservoir concentration varied with time. The concentration data, together with the initial concentrations of the ions, were used in the closed-form solution to Fick's second law for diffusion in soil to calculate effective diffusion coefficients for the specific ions. The procedure for the mathematical analysis is presented later in this section. The general procedure for monitoring the concentrations in the reservoir included the following steps:

1. The temperature, time, and the volume readings of the burets (for the diffusion test and for evaporation) were recorded.
2. The parafilm was removed from the buret.
3. Approximately 25 to 50 ml of liquid were drained by gravity from the sample port in the reservoir into a graduated cylinder.
4. Five to six ml of the liquid were removed from the cylinder with 1-ml or 2-ml pipets to prepare samples for chemical analysis; the remainder of the

liquid was poured into the buret to provide volume change readings for the next sample.

5. The volume of the liquid in the buret was recorded.

6. The buret was re-covered with two layers of parafilm.

The diffusion tests on kaolinite were sampled 28, 42, 57, 81, and 109 days after initiation of diffusion. Tests on Lufkin clay were sampled 14, 35, 50, and 76 days after initiation of diffusion. Tests on Ottawa sand were sampled 15, 40, and 63 days after diffusion started. Initially, it was thought that a substantial amount of time would be required for significant diffusional mass transport to occur. As a result, the first reservoir sample for kaolinite was taken at 28 days after the start of diffusion. However, chemical analysis of this sample revealed that the initial concentration of each ion in the reservoir had decreased by at least 20 percent over this period. Therefore, the initial reservoir sampling period was reduced to about one or two weeks for all of the remaining diffusion tests.

Sectioning of the Soil -- Upon completion of the diffusion stage of the test, the final buret readings were recorded and the liquid in the reservoir was drained into a 250-ml beaker. The last reservoir samples were taken from the beaker, and the pH, electrical conductance, and temperature of the liquid were recorded. The liquid remaining in the reservoir was drained and discarded, and the diffusion cell was disassembled. The final weight of the compaction mold plus the soil was measured so that the total unit weight of the soil could be calculated. The compaction mold with the soil was placed in a load frame immediately following the weight measurement so that the soil could be extruded and sectioned. The load frame, depicted in Figure 5.3, was modified by replacing the proving ring with a 1/2-inch-thick stainless steel plate specially machined to fit the top of the compaction mold. The purpose of the plate was to provide resistance to the compaction mold as the soil was extruded. A 3.95-inch-diameter stainless steel piston, adapted to fit the load frame, was used to apply the pressure to the soil at the bottom of the mold. A dial gauge was mounted to the load frame so that accurate displacements (0.001 inches) of the soil sample could be measured during extrusion.

The clay soils were sectioned for two reasons: (1) to provide a distribution of the water contents existing in the sample and (2) to provide a concentration profile of the specified ions for use in the mass balance and the effective diffusion coefficient determinations. The Ottawa sand fell out of the compaction mold upon separation of the mold from the base plate and, therefore, was not sectioned.

The soil usually was sectioned into slices approximately 0.1 inches in thickness. The slices were spaced at somewhat regular intervals throughout the entire length of the sample. The spacing of the slice was such that 10 slices usually could be recovered from samples in the larger, 1/30-ft³, molds and 5 slices from samples in the smaller, 1/60-ft³, molds. In most instances, the soil between slices was discarded. However, on a few occasions, it was recovered for a water content determination.

The soil samples were sliced with fishing line, a stainless steel knife, and/or an 8-inch X 1-7/16-inch X 1/16-inch stainless steel plate with a sharpened, beveled edge. The fishing line worked well for the kaolinite samples. However, the knife and the sharpened plate had to be used for the Lufkin clay due to its relatively stiff, nonuniform consistency.

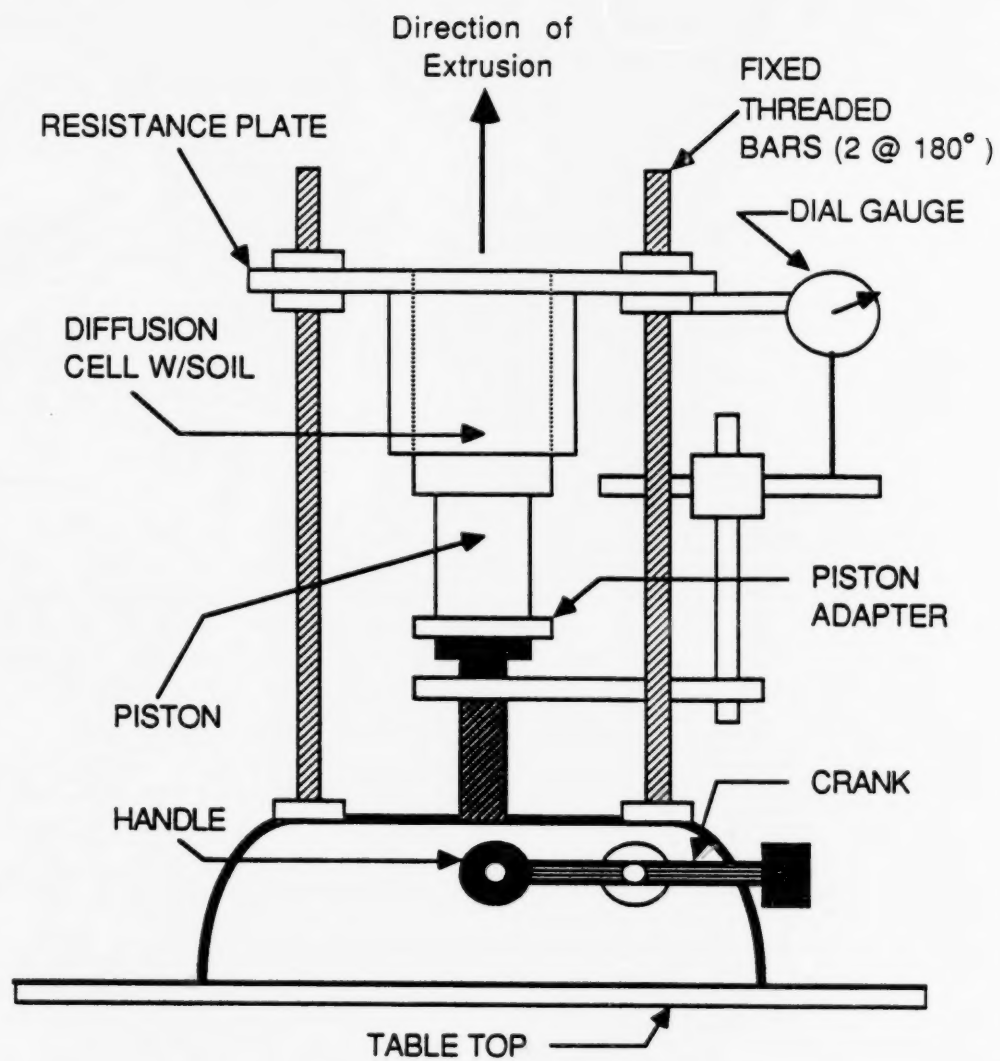


Figure 5.3 Schematic Drawing of Modified Load Frame Used to Section Soil Samples

Portions of the soil from each slice were placed in either one or two pre-weighed 50-ml centrifuge tubes and the weight of the tube plus wet soil was recorded. Each centrifuge tube plus wet soil was then placed into an oven and dried at $110^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for a period of at least 18 hours. After the oven drying period, the weight of each centrifuge tube plus dry soil was recorded. The weights of the soil before and after drying were used to determine the water content of the slice of soil.

In order to determine the ion concentrations in the soil, the ions had to be extracted from the oven-dried soil. Farrah and Pickering (1978) investigated the use of 17 different chemical solutions to extract four heavy metal ions (Pb, Cu, Zn, and Cd) sorbed on kaolinite, illite, and montmorillonite soils. They found that a one millimolar (1 mM) solution of ethylenediaminetetraacetic acid (H_4EDTA) adjusted to a pH of 7.2 worked the best, extracting 100 percent of all the heavy metal ions sorbed onto each of the clays at a pH of 5. For heavy metal ions sorbed onto the kaolinite and montmorillonite clays at a pH of 7, extraction efficiencies were 100 percent for Zn.

Based on the results of the study by Farrah and Pickering (1978), it was decided that a solution containing H_4EDTA would be used to extract zinc from the soil. It should be noted that transition metal cations (including Zn) compete more effectively than certain other cations (e.g., potassium (K^+)) at equal concentrations because transition metal ions have the advantage of shifting electrons to better accommodate ligand (e.g., EDTA) configurations (Bohn et al., 1979, p. 36). For this reason, it was not known whether or not all of the potassium ions sorbed to the clay soil could be extracted with the H_4EDTA solution.

A one millimolar concentration of H_4EDTA was used as the cation extracting solution for kaolinite. The pH of the solution was around 2.8. Therefore, the principal form of EDTA in the solution was $\text{H}_2\text{EDTA}^{2-}$ since the second and third acidity constants of H_4EDTA (i.e., pK_2 and pK_3) are 2.7 and 6.2, respectively (Bohn et al., 1979, p. 37; Stumm and Morgan, 1981, pp. 361-362).

Preliminary mass balance calculations on tests involving kaolinite indicated poor efficiencies with respect to extraction of the cations (Zn^{2+} , and K^+). In an attempt to improve the cation extraction efficiencies, the concentration of the H_4EDTA solution was increased for tests on Lufkin clay to 5 mM. Also, the pH was adjusted with 1.0 M NaOH to around 7.0 so that the number of equivalents of EDTA would be increased from two to three since the fourth acidity constant (pK_4) of H_4EDTA is 10.3 (Bohn et al., 1979, p. 37; Stumm and Morgan, 1981, pp. 361-362).

Initially, it was thought that the H_4EDTA solution could be used to determine the anion concentrations as well as the cation concentrations. However, the H_4EDTA solution was found to interfere with the determination of the chloride and bromide concentrations for the tests on kaolinite. Therefore, it was decided that a separate analysis for anion concentrations should be made for all of the remaining diffusion tests. A separate analysis for anions required that two centrifuge tubes be supplied per slice - one for anions and one for cations. Since the adsorption test results indicated that the specified anions (Cl^- , and Br^-) were not preferentially adsorbed to the soils, it was decided that de-ionized, distilled water (DIDW) could be used as the extracting solution for the anion analysis. This normally is not the case since dilution with DIDW changes the equilibrium chemistry between the sorbed and free concentrations of the ions existing in the soil at the time of breakdown.

After the determination of the water content for each slice of soil from the sectioning stage, the extracting solution was added to the appropriate centrifuge tube (i.e., DIDW was added to one centrifuge tube for anion analysis and H_4EDTA was added to the other centrifuge tube for cation analysis) and the tubes were sealed with the screw-on caps. The weights of the extracting solutions added to each centrifuge tube were recorded. The centrifuge tubes filled with the mixture of soil and extracting solution were then placed in a rotary, end-over-end mixer and mixed at 30 rpm for at least 48 hours. The tubes were then removed from the mixer and centrifuged for 30 minutes at 3000 to 4000 rpm. The supernatant from the centrifuge tubes was pipetted to appropriate containers for chemical analysis.

Calculation of Effective Diffusion Coefficient -- Several procedures can be used to calculate effective diffusion coefficients from the type of test performed for this investigation. A closed-form solution based on measured reservoir concentrations is the most convenient solution and was the primary one used to determine the effective diffusion coefficients reported herein. A second procedure based on analysis of the concentration profile of a solute in the soil at the end of diffusion was also used.

1. Method Based on Reservoir Concentration. The diffusion cell used in the experimental program is represented schematically in Figure 5.4. Diffusion was initiated by introducing simulated leachate into a reservoir of effective length, l , and constant cross-sectional area, A . The effective length of the reservoir was determined by dividing the total volume of leachate introduced into the system (reservoir, top cap, PVC tube, and buret) by the cross-sectional area. After the introduction of the leachate into the reservoir at time zero ($t=0$), mass transport of the chemical constituents in the leachate occurred via molecular diffusion from the reservoir into the soil. The diffusional mass transport resulted in a decrease in the concentrations of chemicals forming the simulated leachate in the reservoir as a function of time. Since the bottom of the cell was closed during the diffusion stage of the test, none of the mass of the diffusing constituents entering the soil at the soil-reservoir interface could exit the soil at the bottom of the cell. Therefore, the initial and boundary conditions were:

$$\begin{aligned} \text{Initially:} \quad & c(0 \leq x \leq a, t=0) = 0 \\ & c(a \leq x \leq a+l, t=0) = 0 \end{aligned}$$

$$\text{Boundary Conditions: } \frac{\partial c(x=0, t>0)}{\partial x} = 0$$

$$c(a \leq x \leq a+l, t>0) = f(t)$$

where c indicates concentration of a solute, x represents position, and t indicates time. The second boundary condition is a flux-controlled boundary condition.

There are several closed-form solutions of Fick's second law for simultaneous diffusion and adsorption in soil with the above initial and boundary conditions (e.g., see Crank, 1975, pp. 56-58). The primary solution utilized in this study is the one derived by Wilson (1948) and given by Crank (1975, p. 57), or :

$$\frac{M_t}{M_\infty} = 1 - \sum_{m=1}^{\infty} \frac{2a(1+a)}{1+a+a^2q_m^2} \exp\left(\frac{-D^* q_m^2 t}{R_d a^2}\right) \quad 5.1$$

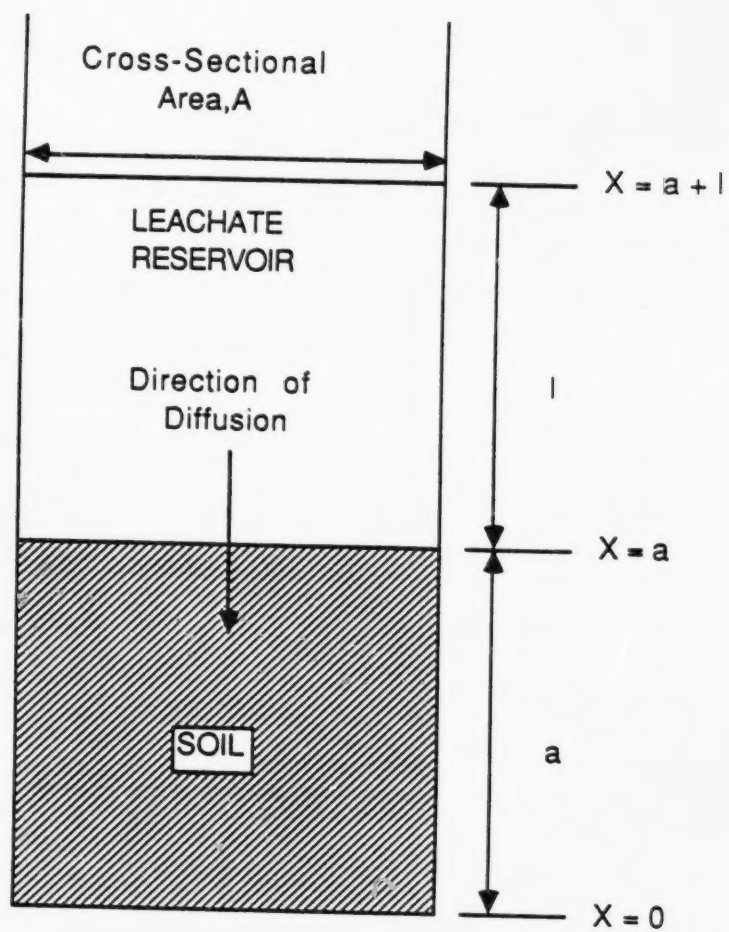


Figure 5.4 Geometry of Diffusion Cell

where M_t is the total mass of a particular solute in the soil at any time t after the start of diffusion and M_∞ is the corresponding mass at infinite time. In Eq. 5.1, the q_m 's are the non-zero positive roots given by :

$$\tan(q_m) = -\alpha q_m \quad 5.2$$

where α is a coefficient that is a function of the diffusion cell geometry, the volumetric moisture content of the soil, and the retardation coefficient of the particular solute (R_d), or :

$$\alpha = \frac{l}{\theta R_d a} \quad 5.3$$

The complete derivation for Eq. 5.1 for a saturated soil is provided in Appendix I of Shackelford (1988), and some roots of Eq. 5.2 are provided in Appendix II of Shackelford (1988).

The assumptions inherent in the use of Eq. 5.1 are as follows: (1) the effective diffusion coefficient, D^* , is constant; (2) the rate of adsorption of solutes by soil is very fast compared with the rate of diffusion; (3) the distribution between the sorbed and free solute concentrations can be described by a linear, constant coefficient of proportionality; and (4) the volumetric moisture content (or total porosity) and density of the soil are constant.

A short computer program (<100 lines) was written to solve Eq. 5.1 for the effective diffusion coefficient, D^* . The required input data included the cell geometry (a, l, A), the volumetric moisture content (θ), the retardation coefficient of the solute (R_d), the reservoir volume ($VR = Al$), the initial concentration of solute i in the reservoir (c_0), and the concentration of solute in the reservoir at elapsed time t (c_t).

The computer program utilized an iterative procedure to solve for D^* . First, a value for D^* was assumed and the series summation on the right side of Eq. 5.1 was calculated. Second, the series summation was subtracted from one minus the left side (i.e., M_t/M_∞) to determine a residual value. Based on the sign of the residual value, the assumed value of D^* was either increased or decreased and the procedure was repeated. When the absolute value of the residual was less than 1.0×10^{-9} , the assumed D^* value was accepted as the solution to Eq. 5.1. The series summation on the right side of Eq. 5.1 required the determination of the non-zero positive roots, q_m . Usually, it was found that only one or two terms were required in the series summation to provide the required accuracy. As a result, the entire iteration procedure converged very rapidly.

2. Method Based on Concentration Profile. The distribution of concentration of a diffusing ion was measured at the end of a diffusion test by sectioning the soil and extracting the ions of interest. Plots were prepared of concentration versus depth. The computer program POLLUTE 3.3 (Rowe and Booker, 1984; and Rowe, Booker, and Caers, 1984) was used to compute concentration profiles for the test regime. Program POLLUTE 3.3 employs a "semi-analytical" solution to the one-dimensional advection-dispersion equation using the method of Laplace transform and numerical inversion. The principal assumptions are that Fick's laws of diffusion apply and that the adsorption isotherm is linear over the range of concentration of interest. The effective diffusion coefficient was adjusted until a best fit (by eye) was obtained between the computed and measured concentration profile at the end of a diffusion test.

COLUMN TESTS

Test Program

The objective of the column tests was to develop data on the transport of inorganic chemicals through compacted clay soils. The variables included in the column tests were (1) hydraulic gradient, (2) type of soil, (3) type of tracer, (4) concentration of tracer, (5) adsorption or desorption of a tracer from the soil, and (6) presoaking of a compacted soil specimen.

The column test program is summarized in Table 5.2. At least two replications were used in each series of tests.

A range of hydraulic gradients from 1 to 50 was selected for this investigation to study the transport of solutes through compacted soils. The gradients chosen in this program were intended to cover a range over which flow would be dominantly diffusional (lowest gradient) to dominantly advective (highest gradient).

For kaolinite soil columns, gradients of 1, 5, and 20 were applied for presoaked samples, and gradients of 1 and 5 for nonsoaked samples. For Lufkin soil columns, gradients of 20 and 50 were applied to both presoaked and nonsoaked samples. The gradient of 20 was chosen as the lowest practical gradient to produce a sufficient quantity of flow through the relatively impermeable Lufkin soil. The gradient of 50 was chosen to provide larger flow quantities.

Two concentrations of tracer were used (Table 5.2). Where time permitted, both sorption and desorption from the soil column were studied. Most soils were presoaked to eliminate soil suction as a test variable, but some columns were not soaked prior to introducing the tracers.

Equipment

The experimental equipment for a column test included three key components: a permeameter, a hydraulic system to control the hydraulic head and to measure the quantity of inflow, and an effluent collector.

Permeameter -- Permeameters have been used by scientists and engineers to measure the hydraulic conductivity of soils for many years. At the beginning of this program, two types of permeameters were considered for the column tests -- fixed-wall and flexible-wall permeameters. The characteristics of both permeameters are documented by Daniel, Anderson, and Boynton (1985).

Several problems were expected with the use of flexible-wall permeameters for this study. First, the latex membrane that confines the soil specimen is susceptible to deterioration over long testing times. Also, the tracers can diffuse through the membrane from the soil into the surrounding water, or vice versa, although the diffusional problem can be minimized by wrapping a thin sheet of aluminum foil around the soil sample or using a different (less permeable) type of membrane (Daniel et al., 1984). Two porous stones and the tubing lines in a flexible-wall permeameter add a significant amount of space to the test system, which will be superposed on the soil pore space. This additional space will change the results of a column test, e.g., by delaying breakthrough of tracers.

Table 5.2 Column Test Program

Type of Soil	Hydraulic Gradient	Presoaked or Nonsoaked	Adsorption or Desorption	Tracers	Tracer Concentration	Sample Column	Repetitions
Kaolinite	1	Presoaked	Adsorption	ZnCl ₂ & KBr	0.01N	KL-01,-04,-14,-18	4
Kaolinite	1	Nonsoaked	Adsorption	ZnCl ₂ & KBr	0.01N	KL-09,-14,-18	3
Kaolinite	5	Presoaked	Adsorption	ZnCl ₂ & KBr	0.01N	KL-03,-08,-12,-15,-17	5
Kaolinite	5	Nonsoaked	Adsorption	ZnCl ₂ & KBr	0.01N	KL-10,-15,-17	3
Kaolinite	5	Presoaked	Adsorption	ZnCl ₂ & KBr	0.001N	KL-11,-16	2
Kaolinite	5	Presoaked	Desorption	ZnCl ₂ & KBr	0.01N	KL-08,-10	2
Kaolinite	10	Presoaked	Both	ZnCl ₂ & KBr	0.01N	KL-2	1
Kaolinite	20	Presoaked	Adsorption	KBr	0.01N	KL-02,-05,-12	3
Kaolinite	20	Presoaked	Desorption	KBr	0.01N	KL-02,-05	2
Lufkin	20	Presoaked	Adsorption	ZnCl ₂ & KBr	0.01N	LL-01,-12	2
Lufkin	20	Nonsoaked	Adsorption	ZnCl ₂ & KBr	0.01N	LL-06,-13	2
Lufkin	50	Presoaked	Adsorption	ZnCl ₂ & KBr	0.01N	LL-02,-11	2
Lufkin	50	Nonsoaked	Adsorption	ZnCl ₂ & KBr	0.01N	LL-05,-14	2

There are other experimental drawbacks with flexible-wall permeameters. Air pressure applied to confine a soil sample and to control pressures on influent and effluent reservoirs is regulated from a centrally-supplied pressure line. A sudden loss in air pressure, which is certainly possible with long-term tests, could destroy a flexible-wall permeability test.

Based on the problems just discussed, the fixed-wall permeameter was chosen for this study. The fixed-wall permeameter has the advantages of simplicity, long-term durability, and no need for an air pressure system.

The fixed-wall permeameter used in this study consisted of two end plates, one reservoir, and one soil column (as shown in Figure 5.5). Clear acrylic plastic was used to construct the end plates and reservoir; this enabled frequent visual observation of soil specimens without disassembling the permeameter. The molds for soil columns were made of stainless steel. Neither stainless steel nor acrylic is likely to react with the tracers or decompose when exposed to the chemicals and soils used in this investigation.

Two holes were drilled and tapped in the top plate. One hole was located at the center of the top plate, which is bevelled inside with the apex at the center. This central hole was mainly used to vent gas bubbles trapped in the permeameter. A valve with septum was attached to the central hole. The septum permitted the insertion of a syringe needle; a syringe was used to suck out the gas bubbles or liquids from the permeameter. The other hole on the top plate was off the center and was connected to an influent line.

The bottom plate was designed to accommodate a thin filter, in addition to an effluent outlet. The filter used in this study had a thickness of only 0.045 inch to minimize the volume of liquid between the effluent end of the soil and the sampling point.

Two different sizes of reservoir were used. The larger reservoir had a capacity of one liter, a diameter of 4 inches, and a length of 5.2 inches. The smaller one had one half of the capacity of the larger one and measured half as long. An influent reservoir was placed on the top of the soil column in a fixed-wall permeameter. The diffusion of a tracer from the reservoir into the soil will decrease the concentration of the tracer in the reservoir. The change in concentration of a tracer was minimized by making the volume of water in the influent reservoir large. The capacity of the reservoir was chosen to be at least two times the void space in a soil column. Also, the liquid in the reservoir was changed every few weeks.

A soil column consisted of a cylindrical, stainless steel mold with the soil compacted in it. Two sizes of compaction molds were used. One is of the size of the usual compaction mold in ASTM standard D-698; the other is one-half of the height of the standard mold. The size of a standard mold is 4 inches (10.2 cm) in diameter and 4.58 inches (11.6 cm) in height. The half-sized mold was designed to minimize the time required for a tracer to pass through a soil column.

In this study, two disks each of No. 100 stainless steel mesh and polyester fabric were used as a filter material at the effluent end of a soil column. The thickness of the filter was only 0.045 inch (0.11 cm). The filter for the column tests was designed to meet the following five requirements:

1. Prevent washout of soil particles,
2. Function with negligible hydraulic head loss in the filter,

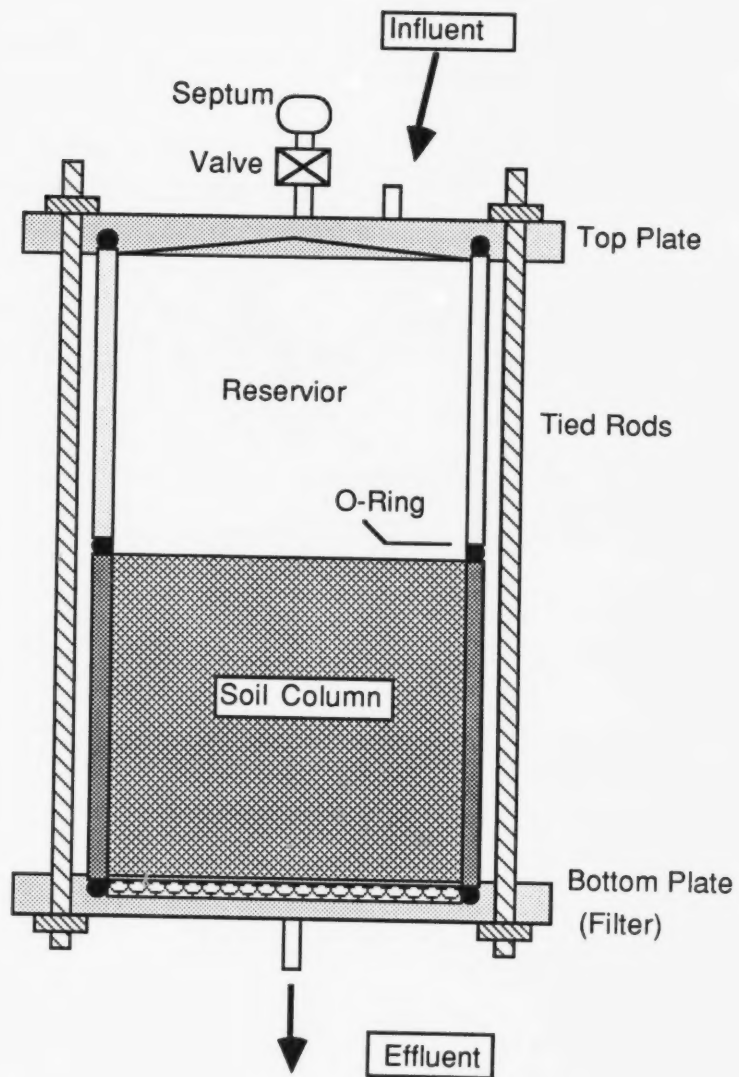


Figure 5.5 Schematic Drawing of the Permeameter Used for Column Tests

3. Provide minimal void space compared with the pore volume in the soil sample,
4. Be stable with time, i.e., not chemically reactive or biologically degradable, and
5. Be more permeable than the soil columns.

The normal filter in hydraulic conductivity tests consists of a piece of thin filter paper and a porous stone. The filter paper prevents the migration of soil particles into the porous stone. The porous stone is a highly permeable material that functions with minimal head loss compared with that in clays. Primarily because of the large volume of water stored in the stone, the design with a porous stone was rejected. The volume of voids in a 0.25-inch-thick porous stone is about 30 ml, and the minimum volume of voids in a soil sample was 200 ml. In this case, a porous stone can increase the volume of test space by 15%. The situation was improved by substituting stainless steel wire mesh for the porous stone.

Filter paper disks were used in the first few tracer tests. After 3 months of permeation with tracers, the filter paper had turned into a yellowish paste which could no longer prevent the washout of particles. Polyester fabric was used in later experiments rather than filter paper. The fabric underwent no noticeable biodegradation.

Hydraulic System -- A constant head was maintained by using a Mariotte bottle (Olson and Daniel, 1981). A 50 ml buret with a plastic tubing of 0.125 inch outside diameter was assembled to function as a Mariotte bottle (as shown in Figure 5.6). The tubing was inserted into the buret through a rubber stopper which sealed the top of buret. The bottom of the buret was connected to a permeameter by clear polyvinyl tubing. The readings on buret were calibrated to account for the space occupied by the plastic tubing in it. A correction factor of 0.92 was obtained from the calibration.

The water pressure in the buret was atmospheric at the tip of the air tube. The buret was lowered or raised to provide a desired hydraulic head for permeation at a particular constant gradient.

The following procedure was used to fill the buret. The stopper was removed, the buret was filled to the zero of reading, and then the stopper was replaced to seal the buret. At this moment, the air tube was filled with solution, too. A syringe was then used to withdraw the water in the air tube through the septum on the permeameter; a syringe could pump out 3 to 4 ml of solution to empty the air tube. Without this procedure, the volume of influent liquid in the buret would be underestimated by up to 8 percent, and the soil column would be temporarily subjected to a higher gradient than the one desired.

The volumetric measurement of both inflow and outflow is important for a tracer test. A significant difference between the volume of inflow and outflow indicates a leak, excessive evaporation, volume change in the soil, or some other anomaly.

Effluent Collector -- The hydraulic discharge rate in the tracer tests ranged from 0.3 to 40 ml/day. An evaporation loss in the effluent collector higher than 10% was regarded as unsatisfactory.

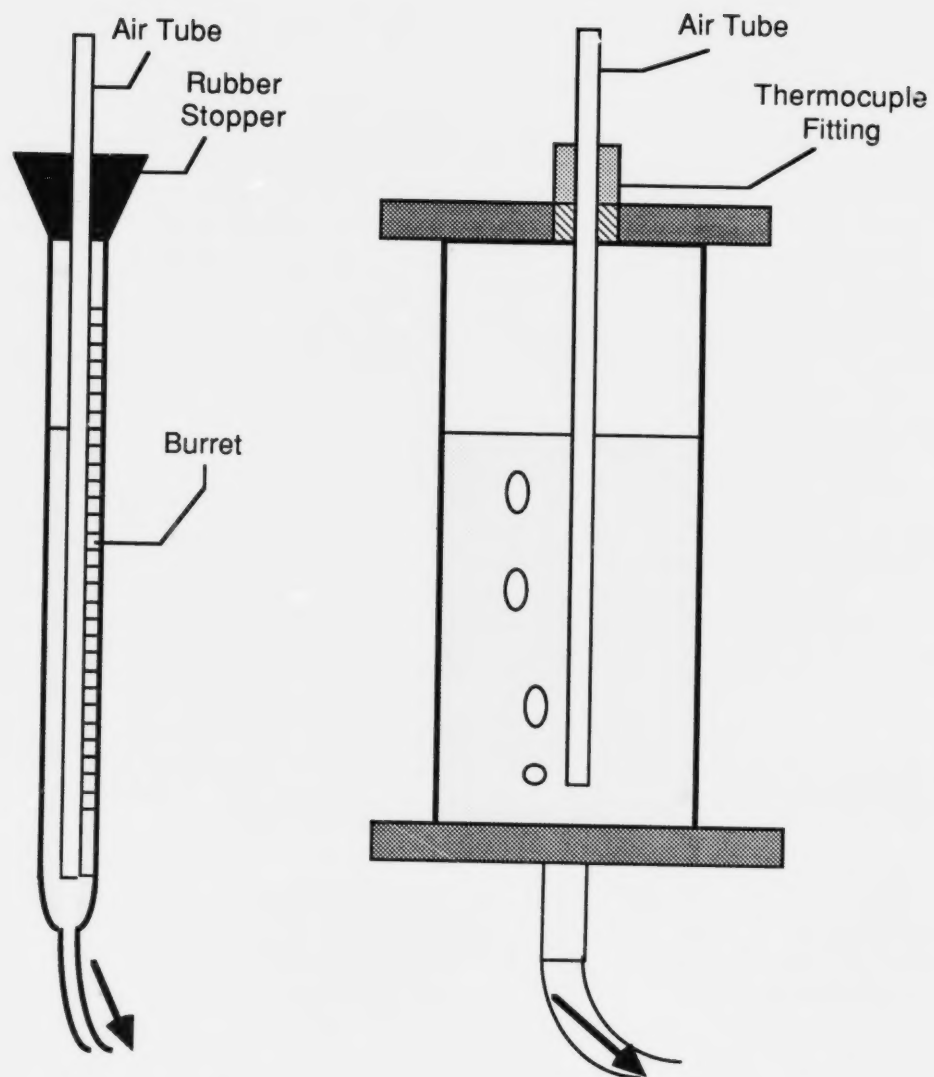


Figure 5.6 Schematic Drawing of Mariotte Bottle

For flow rates higher than 5 ml/day, bottles, beakers, or graduated cylinders were used to receive effluent. These receiving containers were covered with a film of wax paper and pressed upward against the plastic bottom plates of the permeameters to minimize evaporation. The effluent dripped into these collectors from the draining holes beneath the bottom of permeameters. To minimize further evaporation, household plastic wrap was utilized to enclose the space underneath the permeameter, where the effluent collector was placed.

A different arrangement was designed for column tests where the effluent discharge rate was less than 5 ml/day. The idea was to maintain a high relative humidity around the effluent collector to reduce evaporation. A glass beaker and a graduated cylinder were arranged as shown in Figure 5.7. The glass beaker hosted the graduated cylinder and was filled with water to near the rim of the graduated cylinder. Then, a permeameter was placed on the beaker with firm contact. The space beneath the permeameter and above the water surface in the beaker was saturated with moisture. It was this moist space that reduced the evaporation of water in the cylinder.

The area of the water surface in the beaker was 50 times larger than the cross-sectional area of the cylinder. With this system, the evaporation rate of the effluent in the cylinder was reduced to 0.01 ml/day, which is far less than the smallest flow rate of 0.3 mL/day.

Procedures

The column test procedure used in this study consisted of six stages:

1. Preparation of soil specimens,
2. Soaking of soil specimens,
3. Introduction of tracers,
4. Sampling of the effluent liquid,
5. Sectioning of soil specimens, and
6. Chemical analysis of effluent samples and soil water extracts.

Preparation of Soil Specimens -- The preparation of a soil specimen was begun by mixing pulverized air-dried soil with 0.01N CaSO_4 in distilled water until the desired moisture content was obtained. The soil was mixed in a mechanical mixer while the water was sprayed into the soil as a fine mist. The soil was then placed in plastic bags to hydrate for at least 24 hours. This mixing procedure was similar to the one used by Foreman (1984).

After hydration, the soil was compacted according to ASTM standard D-698 (Standard Proctor), Method A. The soil was compacted into two different sizes of cylindrical stainless steel molds. The standard mold was 4.0 inches in diameter, 4.584 inches in height, and 1/30 cu. ft. in volume. The other was one-half of the height of the standard mold.

The soil was compacted in three lifts into the standard mold. Each soil lift received 25 blows from a 5.5-pound hammer dropped from a height of 12 inches above

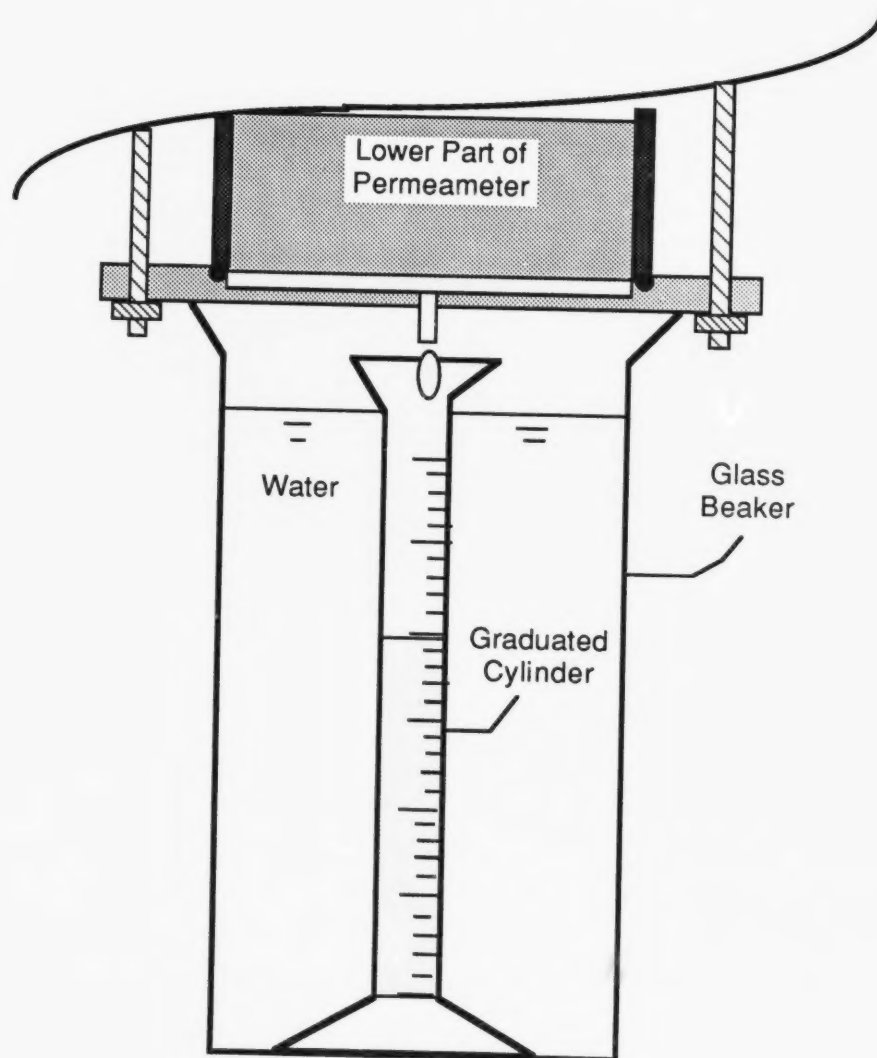


Figure 5.7 Schematic Drawing of Effluent Collector

the soil. The interface between lifts was scarified with a fork to promote bonding. Based on the same energy density, the soil in the half size mold was compacted in two lifts. Each lift received 19 blows. The results showed no significant difference in dry densities of soils in these two molds.

Soaking of Soil Specimens -- After the soil was compacted into a mold, the soil column was immediately assembled into a permeameter to avoid loss of water due to evaporation. Most of the soil columns were then soaked to minimize the influence of suction.

Soaking started when the reservoir of permeameter was filled with 0.01N CaSO_4 . The soaking time for kaolinite was two weeks and four weeks for Lufkin clay. The soaking time was determined on the daily amount of water taken by the soil. A buret was attached to the permeameter to monitor the uptake of water. When the daily uptake was less than 0.5 ml/day, the effect of suction was assumed to be insignificant. It is not assumed that the soil is fully saturated at this time; air bubbles were presumably entrapped in the soil.

In the beginning of this research, the soaking was accomplished by exposing both ends of the soil column to water. Later in this study, the soaking was accomplished by flowing water downward through the soil column.

Introduction of Tracers -- Tracers were introduced by replacing the reservoir liquid with water containing the tracers. Two groups of tracers were selected for this study. Each tracer group has one anionic and one cationic tracer. One group is potassium bromide, the other zinc chloride. A second tracer group served as a backup of the first one when both are introduced at the same time. These two tracer groups could also be applied at two different times. Introduction of secondary tracers at a different time was used to investigate the influence of suction on the transport of a tracer in an unsaturated soil.

Six soil columns in this study underwent tracer desorption tests. The purpose of desorbing the tracers was to examine the reversibility of the sorption process.

The concentrations of tracers in the reservoir were not constant, due to the diffusion of tracers into the pore fluid in the soil column and the adsorption of cationic tracers by clay particles. The change in concentration was monitored by periodically sampling the reservoir liquid. The decrease in concentration was observed in all Lufkin tests and the tests of kaolinite at gradient of one. The decrease was caused by the diffusive flux into soil column from reservoir.

To maintain a reasonably constant concentration, the reservoir liquid was replaced every two to four weeks for three times. After three replacements the concentrations of anionic tracers were within 10 percent of the input concentration. However, the concentrations of cationic tracers in the tests involving Lufkin soil could not be maintained at a constant concentration. In the case of Lufkin clay, the reservoir was not replenished. An initially known mass will be assumed to interpret these test results.

Sampling of Effluent Liquid -- The main information derived from a column test is the breakthrough curve of applied tracers. In order to obtain a complete curve, a minimum of ten more-or-less evenly distributed points were desired.

The volume of one effluent sample was typically 10-15 ml, which was amount needed for chemical analyses. The effluent samples were stored in plastic test tubes. The frequency of sampling depended on the discharge rates from the soil columns. For flow rates greater than 5 ml/day, effluent samples were taken every one tenth of a pore volume for the first two pore volumes, then every one quarter of a pore volume for the rest of the test.

For nonsoaked kaolinite and soils having flow rates less than 2 ml/day, effluent samples were taken every 10 ml or every two weeks for the first pore volume, then by the frequency mentioned in last paragraph.

Sectioning/Extracting Tracers from Lufkin Soil Specimens -- The cationic tracers did not appear at a detectable concentration in effluent from the Lufkin soil even after two years of permeation. This was due to the highly adsorptive capability of Lufkin soil for cations. The Lufkin soil was sectioned to provide a concentration profile.

The soil was extruded from the soil mold, then sectioned into slices of 0.5 inches in thickness with the extruding device shown in Figure 5.3 and a piano-wire saw. At least 5 slices could be obtained from each soil column. The soil slices were oven dried at 105° C for 24 hours to measure the water content and the total amount of water in the soil column. About 0.5 gram of the dry soil from each slice was then taken to determine the cation concentration in the soil.

In order to determine the concentration from dry soil, the cations had to be extracted from the soil. Two agents, 0.01M EDTA (pH=7) and 0.01N HNO₃ (pH=2), were considered as the extractant. A preliminary test was conducted to compare their extracting capabilities. A slice of Lufkin soil from the tracer test was used as one sample to be extracted. The results of the test showed that EDTA extracted 12.6% more zinc than HNO₃ did, and only 2% less potassium. So, EDTA at pH=7 and at a concentration of 0.01M was selected as the extracting solution.

A three-stage extracting procedure was used. Twenty ml of EDTA was added to centrifuge tubes containing 0.5 gm of soil. The centrifuge tubes filled with the mixture of soil and extracting solution were shaken for 30 minutes in a rotary mixer. The tubes were then centrifuged to separate the solution from the soil particles. The supernatant liquid in each tube was decanted. Two more additions of extracting solution of 20 ml were added to the tube and centrifuged; the supernatant was accumulated in the same container from each successive mixing/centrifugation/decanting sequence. About 55 ml extracting solution were recovered from each tube for chemical analysis.

Methods of Data Analysis

Presoaked Soils -- The advection-dispersion equation (Eq. 4.9) was solved by Ogata and Banks (1961) with the technique of Laplace transform for an infinitely long column subjected to step load of solutes. The solution is:

$$c(x,t) = \left(\frac{1}{2}\right) \left[\operatorname{erfc}\left(\frac{x-v_s t}{2\sqrt{Dt}}\right) + \exp\left(\frac{v_s x}{D}\right) \operatorname{erfc}\left(\frac{x+v_s t}{2\sqrt{Dt}}\right) \right] \quad 5.4$$

with the initial condition:

$$c(x,t=0) = 0 \text{ for } x \geq 0$$

and the boundary conditions:

$$c(0,t) = c_0$$

$$C(\infty,t) = 0$$

where erfc stands for complimentary error function, which is defined as:

$$\text{erfc}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_0^x \exp(-h^2) dh \quad 5.5$$

The solution was derived on three main assumptions: (a) the porous medium is homogeneous and isotropic, (b) solutes transported due to microscopic velocity variations may be expressed as the product of a dispersion coefficient and the concentration gradient, and (c) the flow in the medium is unidirectional and of constant velocity among the length of the flow field.

The solution was programmed into a computer code. The series expansion of an error function is:

$$\text{erf}(z) = \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n z^{2n+1}}{n! (2n+1)} \quad 5.6$$

The series expansion with 30 terms was used in this study. For arguments greater than 2.8, the series expansion could not provide good accuracy due to roundoff. An asymptotic expansion of an error function was introduced for arguments greater than 2.8. Comparisons between the values of error function calculated by the computer code and the values tabulated by Freeze and Cherry (1979) showed essentially the same values over the range of 0.0 - 3.0.

In the computer code, the time in the solution also could be expressed in terms of pore volumes by calculating the amount of discharge at time t and dividing the discharge by the experimentally determined pore volume of soil column. Experimental breakthrough curves expressed in relative concentration (c/c_0) versus pore volumes of flow were analyzed by the use of Ogata and Banks' solution, varying the hydrodynamic dispersion coefficient and the effective porosity. Computed and measured curves were matched by eye until a best fit was obtained.

The use of the infinite boundary condition in Ogata and Banks' solution for experimental breakthrough curves obtained from finitely long soil columns was carefully examined by Parlange and Starr (1975). The boundary conditions of $\partial c / \partial x = 0$ @ $x = L$, (where L is the length of soil column), was used in Parklange and Starr's analysis. An approximate solution with a finite boundary was derived to compare the accuracy of Ogata and Banks solution. Parklange and Starr concluded that the Ogata and Banks' solution is adequate to analyze the breakthrough curve of a finite column but yields a less precise estimate of the profile within a column.

Unsaturated Soils -- SOILINER is the computer code that is recommended by EPA for analysis of the time of travel of a constituent through a soil liner. SOILINER is a finite-difference approximation of the nonlinear equation for one-dimensional, unsaturated flow in the vertical dimension.

In SOILINER, a particle tracking algorithm is utilized to determine the time required for a particle to pass through the liner. The effects of dispersion are not accounted for; breakthrough is directly associated with the average linear velocity of migrating contaminants. The particle is initially positioned at the liner surface, and the subsequent movement is then determined from velocity data generated by SOILINER for each time step. SOILINER then numerically integrates the velocity with time to determine the distance traveled over a time period.

For the numerical solution of the governing equation for vertical flow in an initially unsaturated soil, the soil moisture content, θ , and the hydraulic conductivity, k , must be determined. Twelve moisture characteristic curves are available in SOILINER to relate soil moisture content with suction pressure. After close examination, one curve provided in SOILINER appeared to match the soils used in this study better than the others. The moisture-characteristic curve of this soil was described by:

$$\frac{\theta - \theta_r}{\theta_s - \theta_r} = \left(1 + \frac{(\ln \psi)^4}{a}\right)^{-1} \quad 5.7$$

where $a = 739$ and ψ = suction head in cm, $\theta_r = 0.124$, and the hydraulic conductivity was described by:

$$k = k_s \frac{h}{b + \psi^n} \quad 5.8$$

where $b = 124.6$, $n = 1.77$, k_s = hydraulic conductivity at saturation.

DATA QUALITY

Quality Assurance Plan

A quality assurance (QA) plan was developed for this project. It was recognized in the development and implementation of the QA plan that the research involved the use of non-standard experimental techniques to measure hydraulic conductivity, diffusion coefficients, and time of travel of solutes through soil columns. In addition, it was recognized that the compacted soil specimens themselves inevitably had some variability. Efforts to ensure quality in data collection focused on careful collection of data, evaluation of data plots for inconsistencies, and, where possible, comparison of results obtained from this project with results from other projects.

The chemical analysis of aqueous samples did involve use of standard methods. An EPA Performance Evaluation Study occurred during the course of the project. In this study, the investigators were sent solutions for chemical analysis by EPA. The actual concentrations of chemicals in the solutions were unknown to the investigators at the time the chemical analyses were made and reported to EPA. Except for measurement of Cl^- concentrations that were slightly too low (about 5% below actual values), the

Performance Evaluation Study indicated measurements within acceptable limits. The Cl^- concentrations were slightly low because an old calibration solution had been used. However, the fact that the measured Cl^- concentrations were slightly low had no influence on the research since the data were analyzed in terms of concentration (c) relative to concentration in the influent reservoir (c_0) -- the c/c_0 ratio was unaffected by the slight error in calibration for Cl^- .

Quality Control Issues

The credibility of data obtained in this investigation can be evaluated in terms of the curve fit to equations derived from transport theory. The precision and accuracy of the measurements cannot be evaluated from the data given for the diffusion tests or column tests even though duplicate experiments were conducted for each soil/constituent combination. Heterogeneity in the soil matrices precludes comparison of data obtained from duplicate experiments.

SECTION 6

RESULTS OF EXPERIMENTS

BATCH ADSORPTION TESTS

Kaolinite

Two combinations of cationic species, potassium and potassium plus zinc (added in equal amounts), were used with kaolinite to develop adsorption isotherms. The isotherm for potassium alone is presented in Figure 6.1. The points in Figure 6.1 represent calculations from direct measurements. The curve plotted in Figure 6.1 corresponds to the curve predicted by the Freundlich isotherm equation (Eq. 4.12). The parameters needed for the Freundlich equation were computed from a least-squares fit of the Freundlich isotherm equation to the data. The Freundlich parameters, along with those computed for the Langmuir equation, are presented in Table 6.1. The correlation coefficient, R , is also given in this table. At low concentrations, the distribution coefficient (K_d) for the nonlinear isotherm is approximately $0.002 \text{ (mg/g)/(mg/L)}$.

The adsorption isotherms for potassium and zinc are presented in Figure 6.2. In this case, potassium and zinc competed for sorption sites. The curves shown in Figure 6.2 were generated from the Freundlich equation with the parameters listed in Table 6.1. Kaolinite had a slightly greater tendency to sorb potassium compared to zinc. At low concentration, K_d is again approximately $0.002 \text{ (mg/g)/(mg/L)}$ for both species.

Lufkin Clay

Adsorption isotherms for potassium and zinc were developed for a solution containing equal initial amounts of potassium and zinc and are shown in Figure 6.3. The curves again represent Freundlich isotherms computed from the parameters listed in Table 6.1. The isotherms show that for a given solution concentration, the amount of adsorbed zinc is significantly larger than the amount of potassium.

At low concentration, the K_d values are approximately 0.01 and 0.1 (mg/g)/(mg/L) for potassium and zinc, respectively. These K_d values are 5 (potassium) and 50 (zinc) times larger for Lufkin clay than for kaolinite. The greater capacity of Lufkin clay to sorb metals, compared to kaolinite, is expected based upon the mineralogy and cation exchange capacity of the two soils.

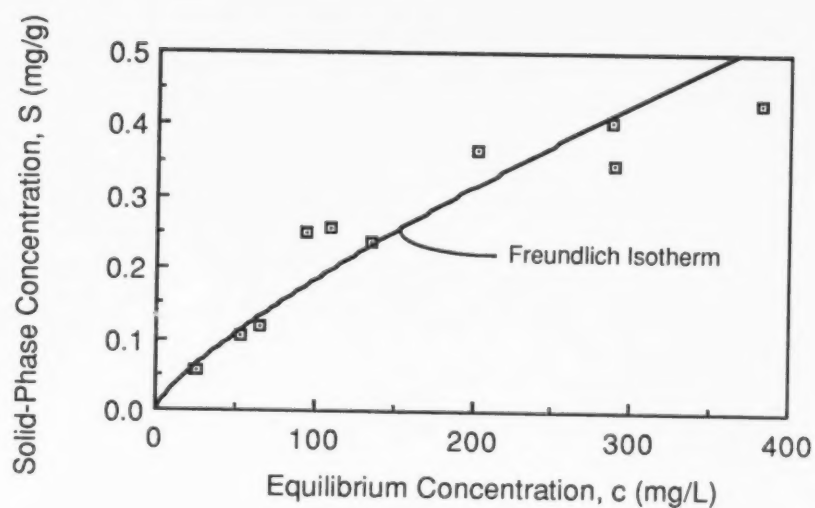


Figure 6.1 Adsorption Isotherm for Potassium Sorbed by Kaolinite

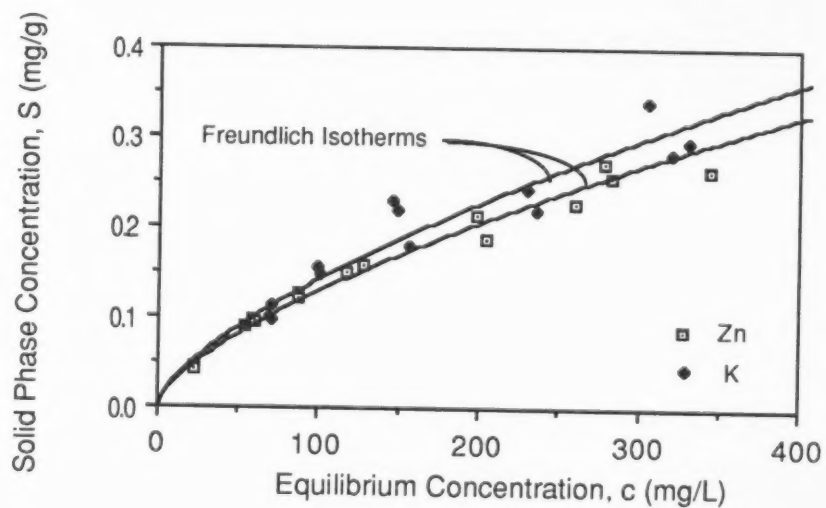


Figure 6.2 Adsorption Isotherms for Zinc and Potassium Sorbed by Kaolinite

Table 6.1 Results of the Curve-Fitting of Data from Batch Tests
Based on Langmuir and Freundlich Isotherms

Type of Soil	Input Cations	Adsorbed Cation	Langmuir Isotherm			Freundlich Isotherm		
			K _L	M	R*	K _f	N	R*
Kaolinite	K	K	0.00225	1.062	0.99	0.0052	0.7743	0.97
Kaolinite	Zn, K	K	0.00251	0.700	0.97	0.0064	0.6715	0.96
Kaolinite	Zn, K	Zn	0.00574	0.379	1.00	0.0060	0.6653	0.99
Lufkin	Zn, K	K	0.00575	2.162	0.99	0.300	0.3705	0.98
Lufkin	Zn, K	Zn	0.070	1.751	0.99	0.513	0.5805	0.98

* R is the reliability factor of regression analysis

* Freundlich Isotherm : $S = K_f \cdot c^N$

* Langmuir Isotherm : $S = \frac{K_L M c}{1 + K_L c}$

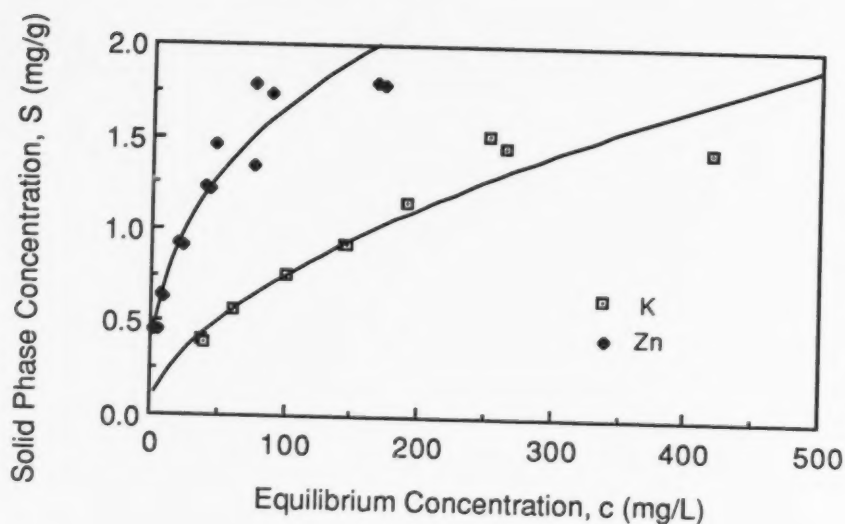


Figure 6.3 Adsorption Isotherms for Zinc and Potassium Sorbed by Lufkin Clay

DIFFUSION TESTS

Effective Diffusion Coefficient

Data from Reservoir Concentration -- Effective diffusion coefficients (D^*) were calculated from the measured change in reservoir concentration over time, as described in Section 5. Several reservoir samples were taken during the course of each test. As a result, several D^* values were calculated for each ion. Due to the scatter in the concentrations, the calculated D^* values tended to vary, as well. All of the D^* values determined from reservoir analyses for a given ion were averaged in order to provide a basis for a comparison of the results.

Plots of concentration of an ion in the diffusional reservoir versus time are presented in Figures 6.4 and 6.5 (kaolinite) and in Figures 6.6 and 6.7 (Lufkin clay). Each figure contains separate plots of the concentration of chloride, bromide, potassium, and zinc versus time for one replication of a given soil. Because two replicates were performed for each soil, there are two figures per soil type. The data points in the figures represent experimentally-determined values; the curves represent the computed values from Eq. 5.1 (the theoretical

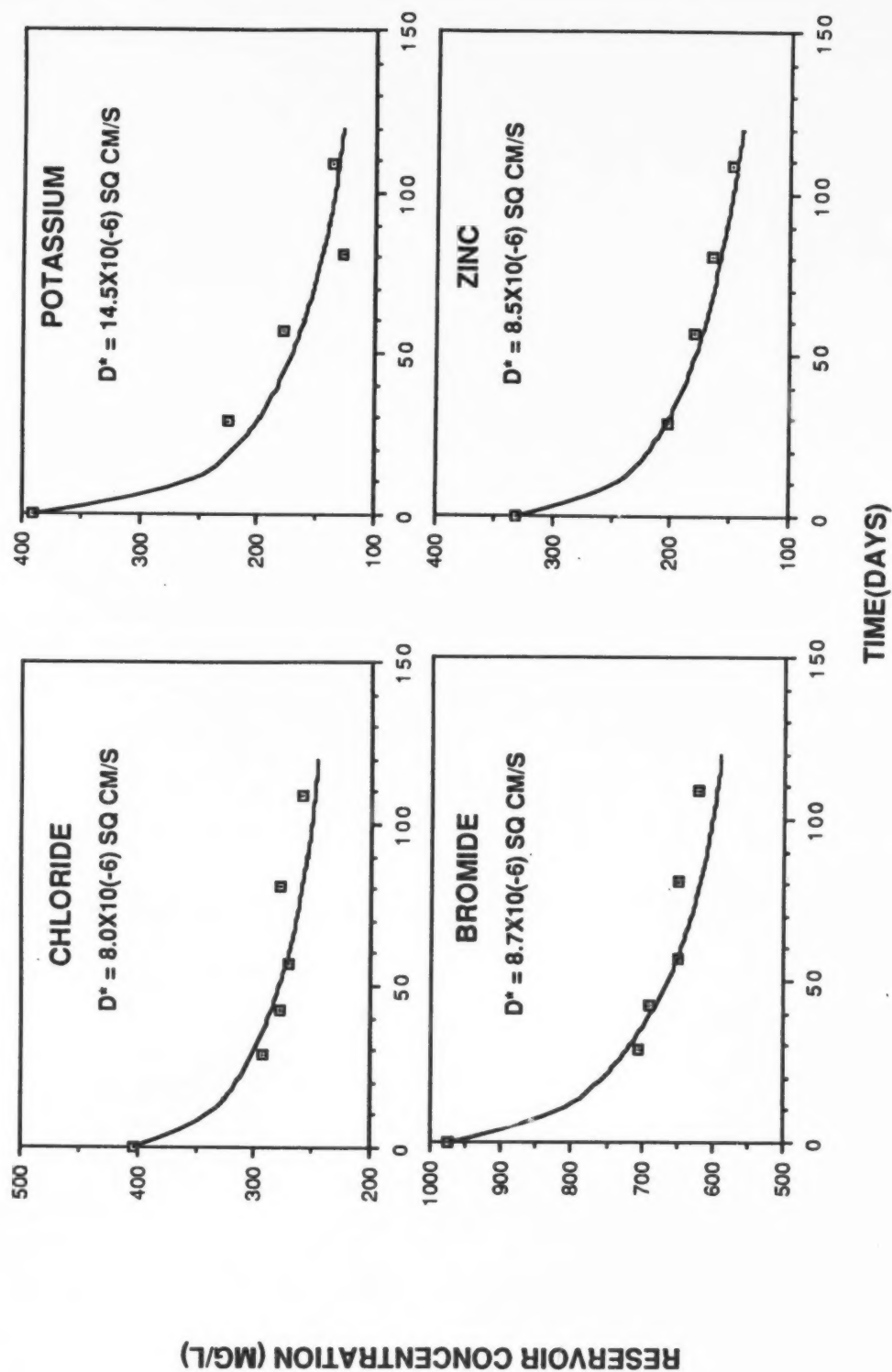


Figure 6.4 Variation of Reservoir Concentration with Time in First Replicate Diffusion Test with Kaolinite

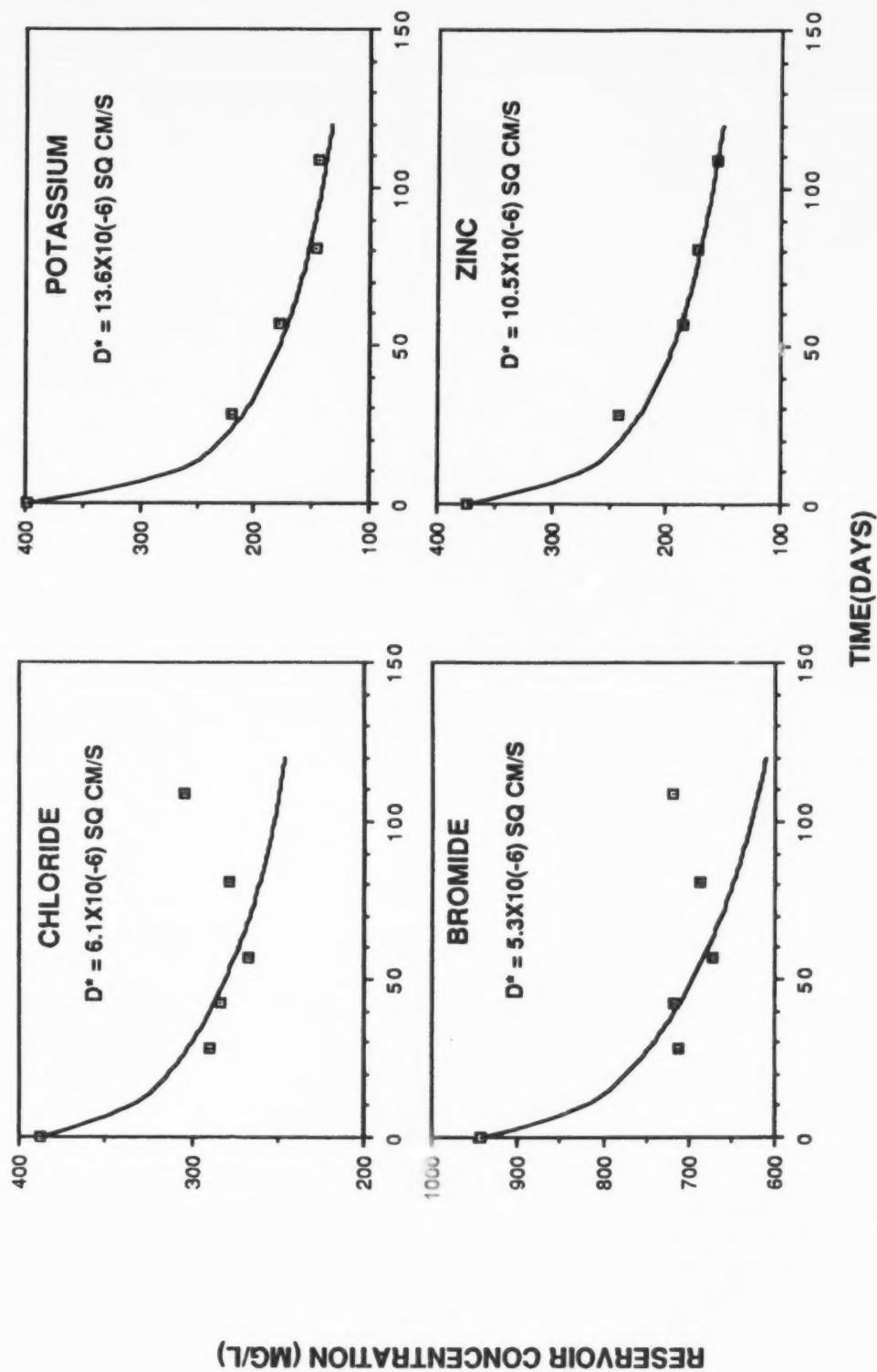


Figure 6.5 Variation of Reservoir Concentration with Time in Second Replicate Diffusion Test with Kaolinite

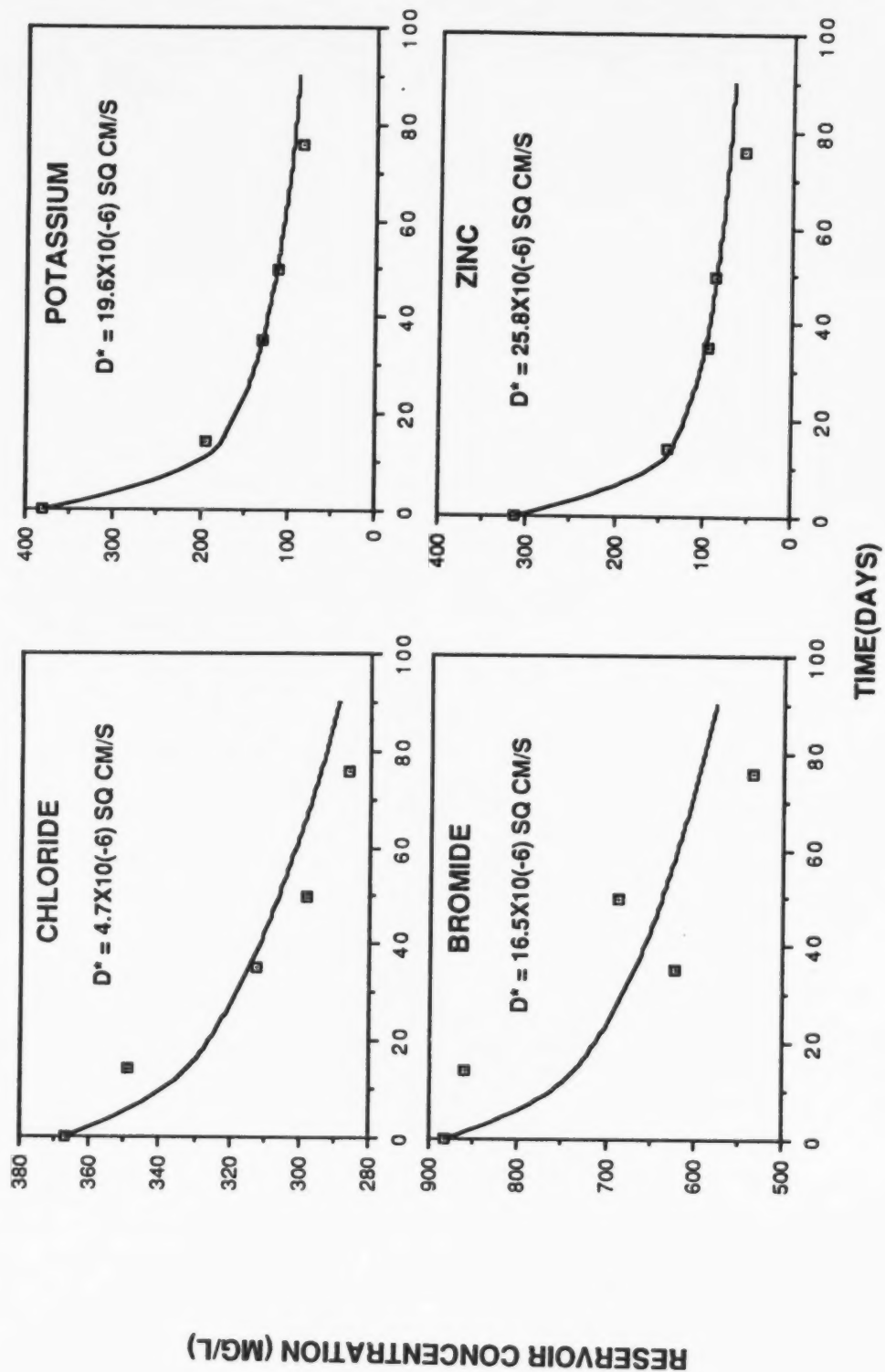


Figure 6.6 Variation of Reservoir Concentration with Time in First Replicate Diffusion Test with Lutkin Clay

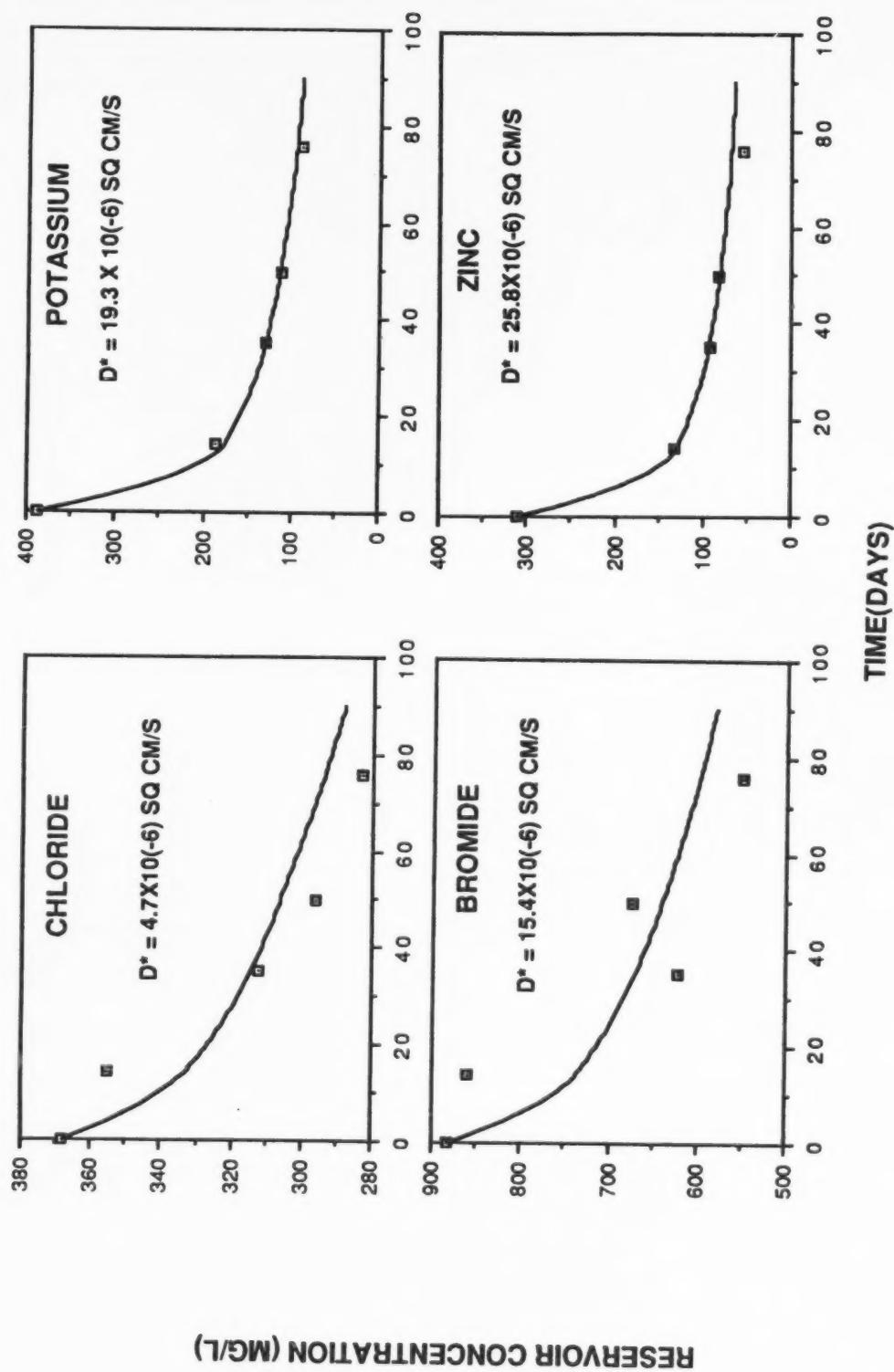


Figure 6.7 Variation of Reservoir Concentration with Time in Second Replicate Diffusion Test with Lufkin Clay

curve based on Fick's first and second laws). The average effective diffusion coefficients are shown in the figures for each ion and are summarized in Table 6.2. The agreement (or lack of agreement) between the experimental points and the theoretical curves provides an indication of how well Fick's laws describe the diffusional process. In general, the agreement between theoretical curves and experimental points is thought to be reasonably good, considering the myriad geochemical parameters that can affect the diffusional process.

No attempt was made to correct the reservoir concentrations for the background ion concentrations measured in the soil. The background ion concentrations were measured on saturation soil extracts that probably do not represent the conditions in the soil in the diffusion tests. Also, some of the background ions in the soil probably diffused into the reservoir during the soaking stage of the tests and subsequently were removed when the soaking solution was replaced by the diffusion liquid. Therefore, the initial concentrations of the ions in the soil samples are unknown. However, the high background chloride concentration measured for Lufkin clay probably affected the diffusion of Cl^- in the tests.

Data from Concentration Profiles -- Some test specimens were sectioned after the diffusion test was complete. The effective diffusion coefficient was calculated from the concentration profile in the soil. The procedure for computing D^* was described in Section 5. Trial values of D^* were employed to compute the theoretical concentration profile, and the D^* value was adjusted until a good fit (by eye) was obtained.

Concentration profiles for chloride, bromide, and zinc are shown in Figures 6.8 and 6.9 (kaolinite) and in Figures 6.10 and 6.11 (Lufkin clay). The points in these figures represent experimental data, and the curves represent calculated concentration profiles at the end of the diffusion test based on the D^* values shown in the figures and Fick's second law. Again, the quality of agreement between the theoretical curves and experimental data provides an indication of how well Fick's law applies to diffusion of solutes in soil. The effective diffusion coefficients computed from the concentration profiles are summarized in Table 6.3. Diffusion coefficients were not computed for K^+ because the EDTA solution produced incomplete extraction of K^+ , and the concentration profiles for K^+ were not adequate for computation of D^* .

Analysis of Results -- The effective diffusion coefficients for each soil have been averaged for the two replicates, and the averages are reported in Table 6.4. The D^* 's range from $1 \times 10^{-6} \text{ cm}^2/\text{s}$ to $26 \times 10^{-6} \text{ cm}^2/\text{s}$, which is a range of approximately 1 order of magnitude.

The effective diffusion coefficient for Cl^- and Br^- should have been about the same for all soils. For kaolinite, this was the case. For Lufkin clay, the D^* value for Cl^- is much lower than for Br^- (Table 6.4), based on reservoir concentrations. However, Lufkin clay contained Cl^- in the natural pore water at a

Table 6.2 Effective Diffusion Coefficients from Reservoir Concentrations

Type of Soil	Replication	Effective Diffusion Coefficient, D^* ($\text{cm}^2/\text{s} \times 10^6$)			
		Chloride	Bromide	Potassium	Zinc
Kaolinite	1	8.0	8.7	14.5	8.5
Kaolinite	2	6.1	5.3	13.6	10.5
Lufkin Clay	1	4.7	16.5	19.6	25.8
Lufkin Clay	2	4.7	15.4	19.3	25.8

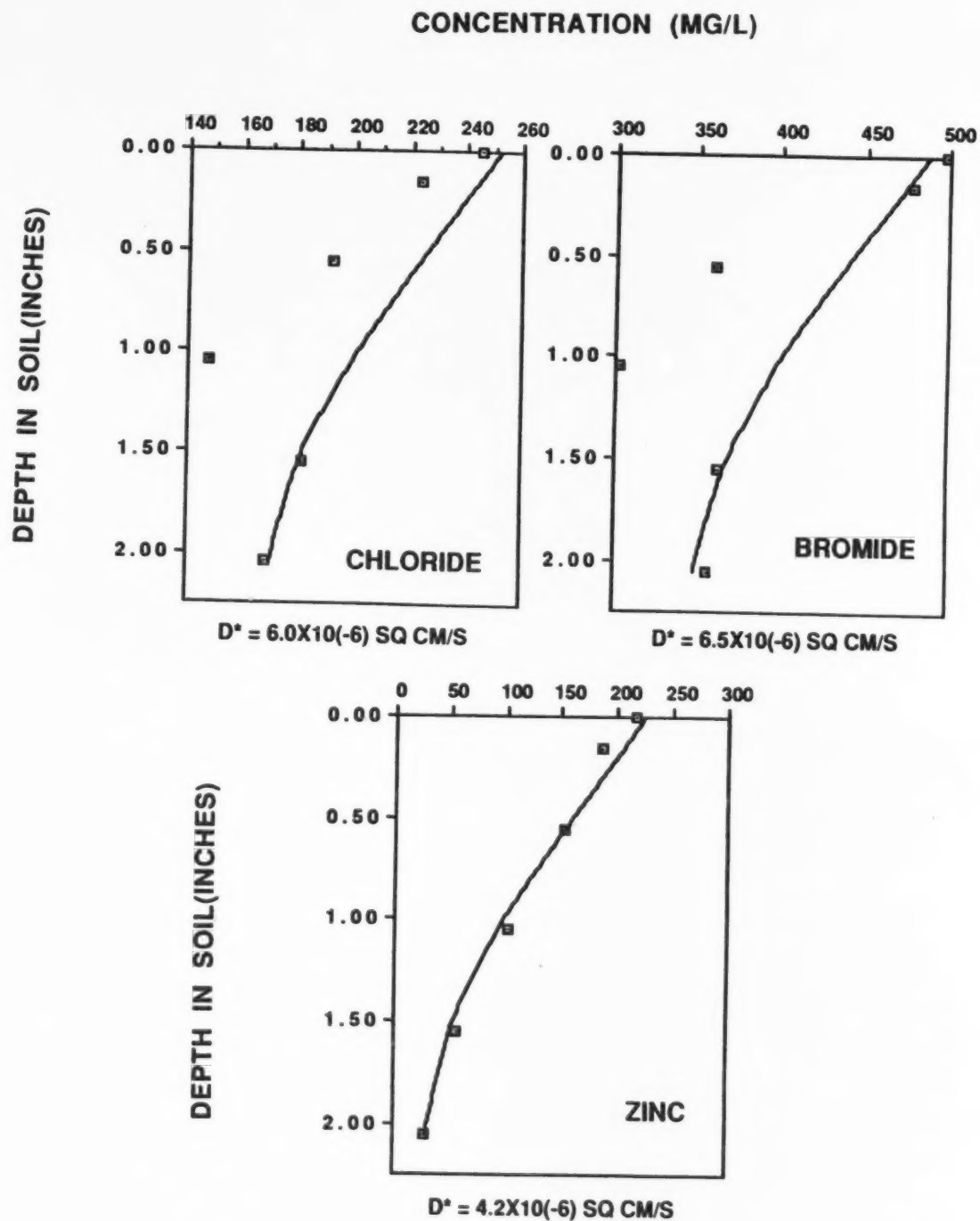


Figure 6.8 Concentration Profiles at End of 109-Day Diffusion Test on First Replicate Test on Kaolinite

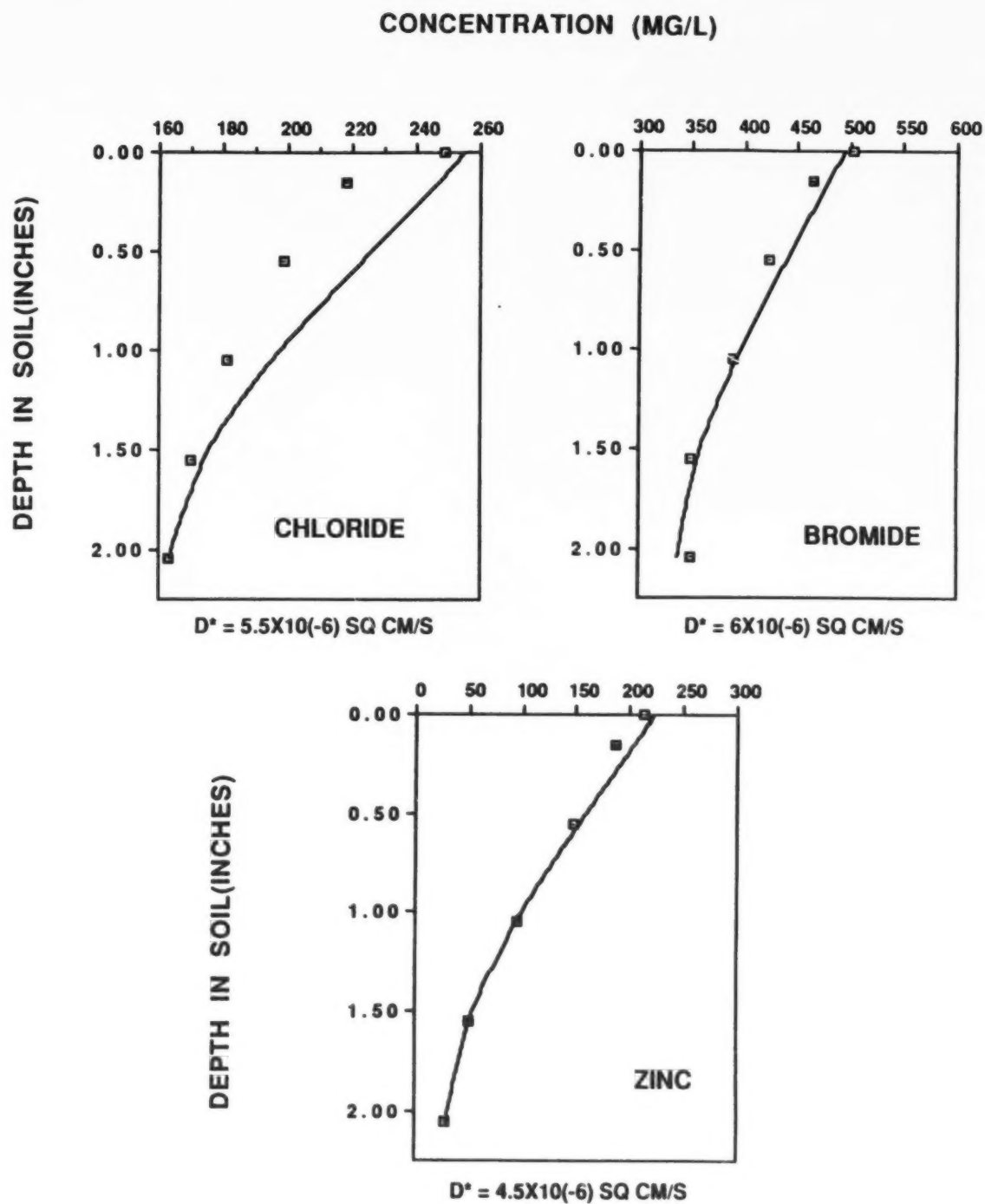


Figure 6.9 Concentration Profiles at End of 109-Day Diffusion Test on Second Replicate Test on Kaolinite

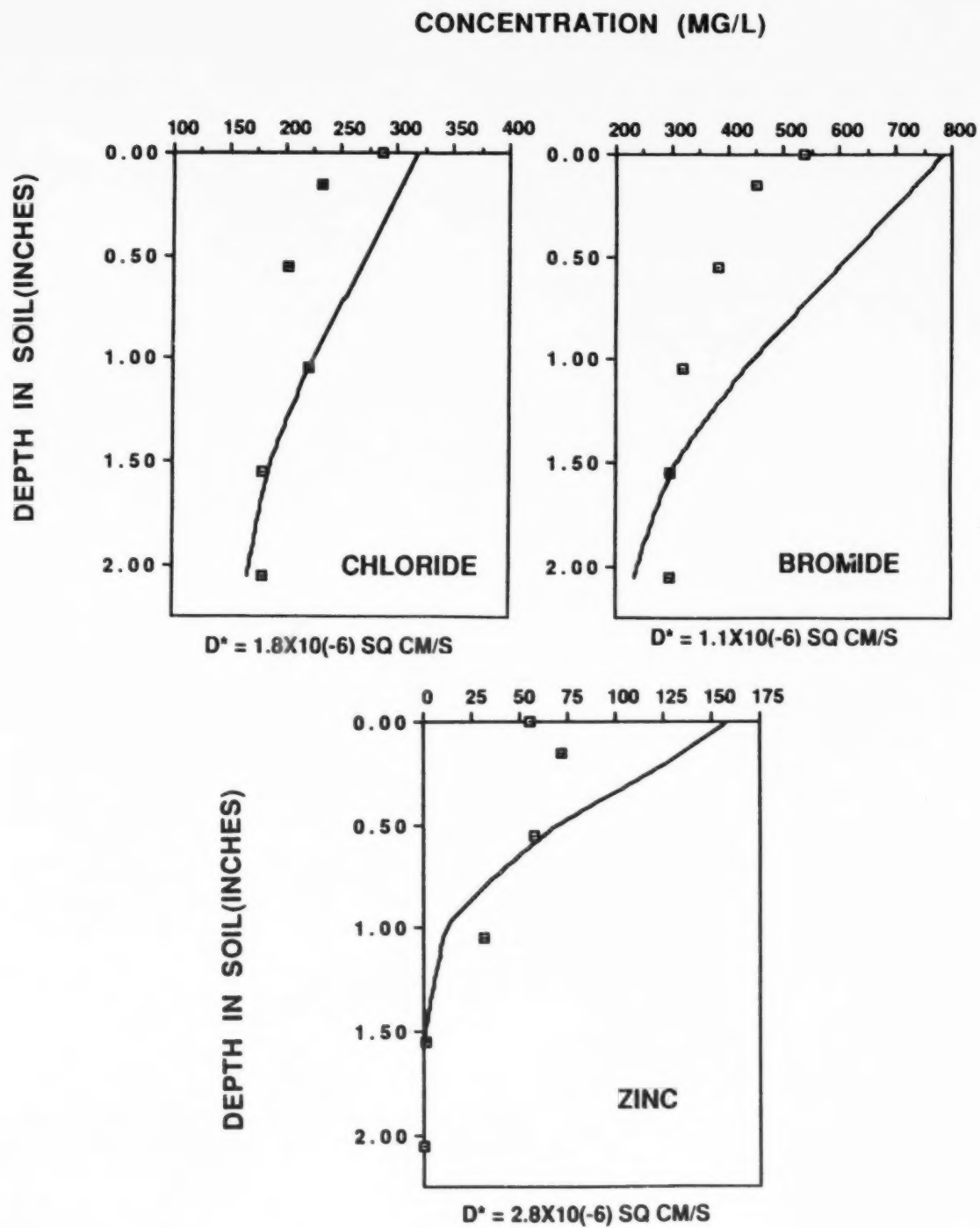


Figure 6.10 Concentration Profiles at End of 76-Day Diffusion Test on First Replicate Test on Lufkin Clay

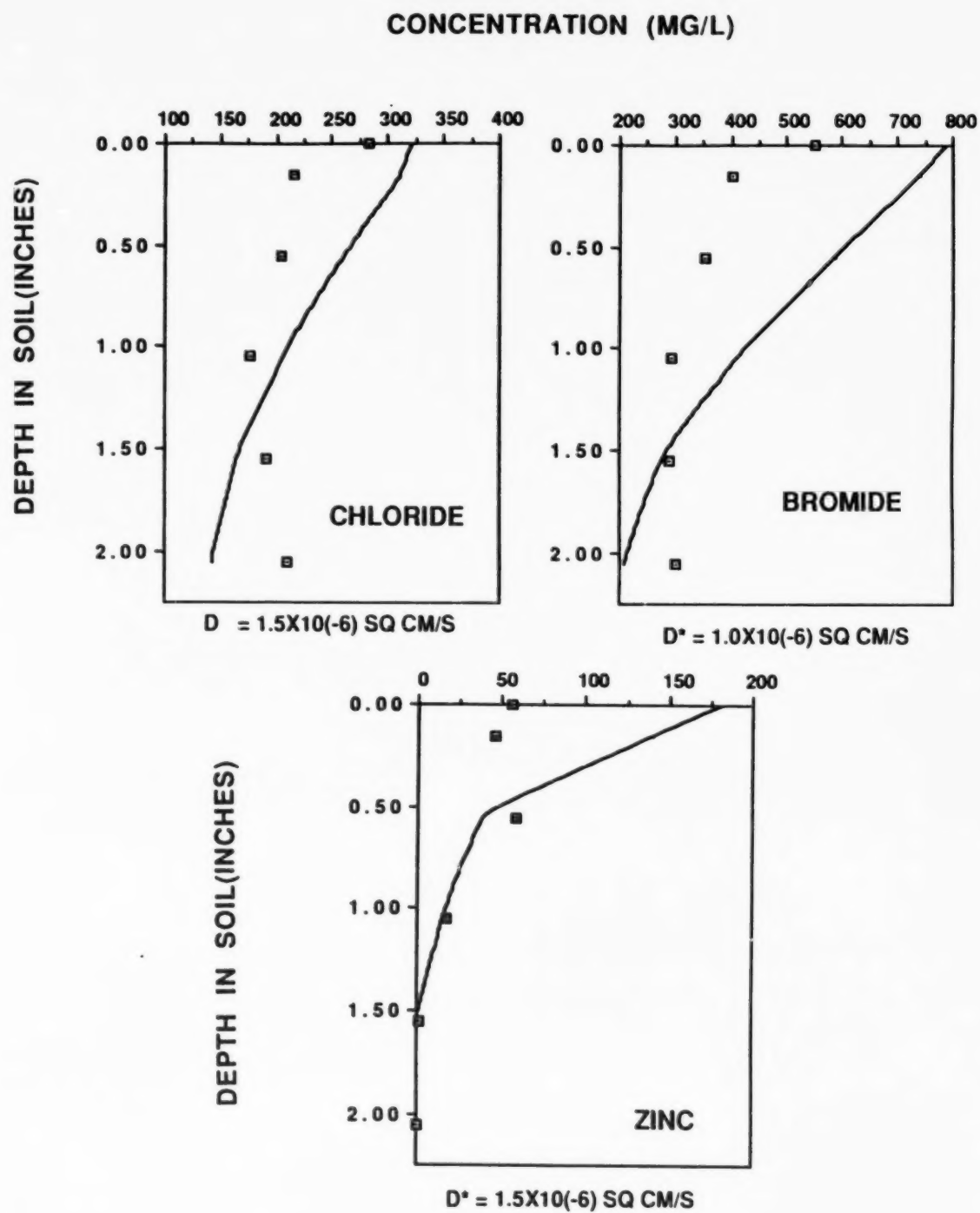


Figure 6.11 Concentration Profiles at End of 76-Day Diffusion Test on Second Replicate Test on Lufkin Clay

Table 6.3 Effective Diffusion Coefficients Computed from Sectioning

Type of Soil	Replication	Effective Diffusion Coefficient, D^* ($\text{cm}^2/\text{s} \times 10^6$)			
		Chloride	Bromide	Potassium	Zinc
Kaolinite	1	6.0	6.5	- -	4.2
Kaolinite	2	5.5	6.0	- -	4.5
Lufkin Clay	1	1.8	1.1	- -	2.8
Lufkin Clay	2	1.5	1.0	- -	1.5

Table 6.4 Summary of Diffusion Coefficients

Tracer	Free Solution	Diffusion Coefficient, $\text{cm}^2/\text{s} \times 10^6$			
		Kaolinite		Lufkin Clay	
		Reservoir	Sectioning	Reservoir	Sectioning
Cl^-	20	7	6	5	2
Br^-	21	7	6	15	1
K^+	20	14	--	19	--
Zn^{2+}	7	10	4	26	2

similar concentration to that in the diffusional reservoir. The diffusion data for Cl^- in Lufkin clay are considered invalid for this reason.

The effective diffusion coefficient for Zn^{2+} was much lower when calculated from final profiles of Zn^{2+} in the soil compared to calculations based upon reservoir concentrations. Some Zn^{2+} precipitated from solution, leading to a loss of Zn^{2+} from the reservoir that was not associated with diffusion. The loss of zinc due to precipitation, as well as other potential sinks, was investigated by comparing the mass of a solute lost from the reservoir during the diffusion period to the mass contained within the soil column. The mass within the soil columns was determined by sampling thin sections of the soil, extracting solutes from the sections, plotting the concentration versus depth in the column, assuming a linear distribution of concentration between points, and integrating the plot to determine the mass contained within the soil. Tests on blank columns showed no loss of mass and hence did not reveal any sources and/or sinks associated with the diffusion system. The mass balance data are summarized in Table 6.5.

Several explanations for the imperfect mass balances can be given. First, it is likely that the EDTA extracting solution resulted in poor removal of potassium; as discussed in Section 5, EDTA is known not to be particularly effective at removing monovalent cations from soil. Second, as suggested in the preceding paragraph, zinc likely precipitated, but a thin section of soil at the entrance end of the soil specimens was not taken because the surface of the soil was uneven. It is well known that in the presence of anaerobic bacteria, the sulfur in sulfate (SO_4^{2-}) is reduced to sulfide (S^{2-}), which precipitates metals. The reactions are reviewed by Freeze and Cherry (1979, p. 118). It was evident from visual observations that biological activity occurred; the diffusion water and surface of soil samples were tinted black, yellow, or pale green. Also, a gaseous odor, probably hydrogen sulfide, was detected when the cells were disassembled at the end of a test.

The lack of mass balance for anions may be attributed to chemical complexation or speciation. The computer program REDEQL2 (McDuff and Morel, 1973) was used to investigate speciation. The analyses indicate that approximately 17% of the Cl^- and 13% of the Br^- was present in the form of complexed cations, e.g., ZnCl^+ and ZnBr^+ . These complexed cations were probably not removed by distilled water, which was used to extract anions for determining the mass of an anion in the soil. While complexation does not explain all of the mass balance discrepancy for anions, complexation certainly was a significant cause for mass balance differences.

Another interesting aspect of the data shown in Table 6.4 is that the order of the effective diffusion coefficients for the cations in the tests with Lufkin clay is almost exactly opposite of what is expected based on the results of the batch-equilibrium tests. In the batch tests on Lufkin clay, zinc was much more strongly sorbed by Lufkin clay than potassium (Figure 6.3), but the effective diffusion coefficient for zinc is higher than that of potassium for Lufkin clay. The discrepancy is attributed to the different conditions in the diffusion test relative to

Table 6.5 Mass Balance

Type of Soil	Replication	Percent Difference in Mass Balance (See Note 1)			
		Cl ⁻	Br ⁻	K ⁺	Zn ²⁺
Kaolinite	1	15	47	44	46
Kaolinite	2	39	ND	43	52
Lufkin Clay	1	46	78	86	44
Lufkin Clay	2	48	78	86	52

Notes:

1. $\text{Percent Difference} = \frac{\text{MR} - \text{MS}}{\text{MR}} \times 100\%$

where MR = mass lost from reservoir at end of diffusion

MS = mass in soil at end of diffusion

2. ND = no data or insufficient data

the batch equilibrium tests. The soils in the diffusion tests were soaked with 0.01 N CaSO_4 over a period of several weeks, which is much greater than the 48 hours for the batch equilibrium tests. The soils in the diffusion tests were essentially calcium-saturated before the cations from the diffusional solution diffused into them. This was probably not the case in the batch-equilibrium tests, where more-or-less equal competition between all of the cation species is expected. Under the condition of calcium saturation of the soil, potassium (K^+), a monovalent cation, is expected to compete much less favorably than the divalent cations (e.g., Zn^{2+}) for the exchange sites; therefore, the D^* value for K^+ should be relatively greater than one or more of the other cations.

Tortuosity Factor

As discussed earlier, for a conservative (nonreactive) tracer, it is expected that:

$$D^* = \tau D_0 \quad 6.1$$

where τ is a tortuosity factor. Tortuosity factors (τ) can be calculated using the measured effective diffusion coefficients, D^* , for the anions with their respective diffusion coefficients, D_0 , in free solution, based on Eq. 6.1. Since the value of D_0 for the permeant liquid used in this study is unknown, the value of D_0 at infinite dilution, shown in Table 6.4, was used instead. For kaolinite, the calculated tortuosity (τ) is 0.29 to 0.35, which, as discussed in Section 4, is within the range reported in the literature for soil.

For Lufkin clay, only the data for Br^- should be used to calculate τ (since the background concentration of Cl^- in the soil was high). For Br^- , the effective diffusion coefficient ranged from 1 to $15 \times 10^{-6} \text{ cm}^2/\text{s}$ (Table 6.4), depending on how D^* was computed. The computed τ is in the range of 0.05 to 0.71, which, again, is within the range reported in the literature for soil.

COLUMN TESTS

Soil Specimens

Heterogeneousness -- Neither the water content nor the dry density in the soil columns was uniform. Several soil columns were sectioned to measure the distribution of water content and the total amount of water in a soil column. The dry densities in these columns were calculated from the water content based on the assumption of full saturation. Although full saturation was improbable, the assumption permitted an evaluation of the variability of density within a soil column. Typical distributions of water content and dry soil density in both kaolinite and Lufkin clay columns are presented in Figure 6.12.

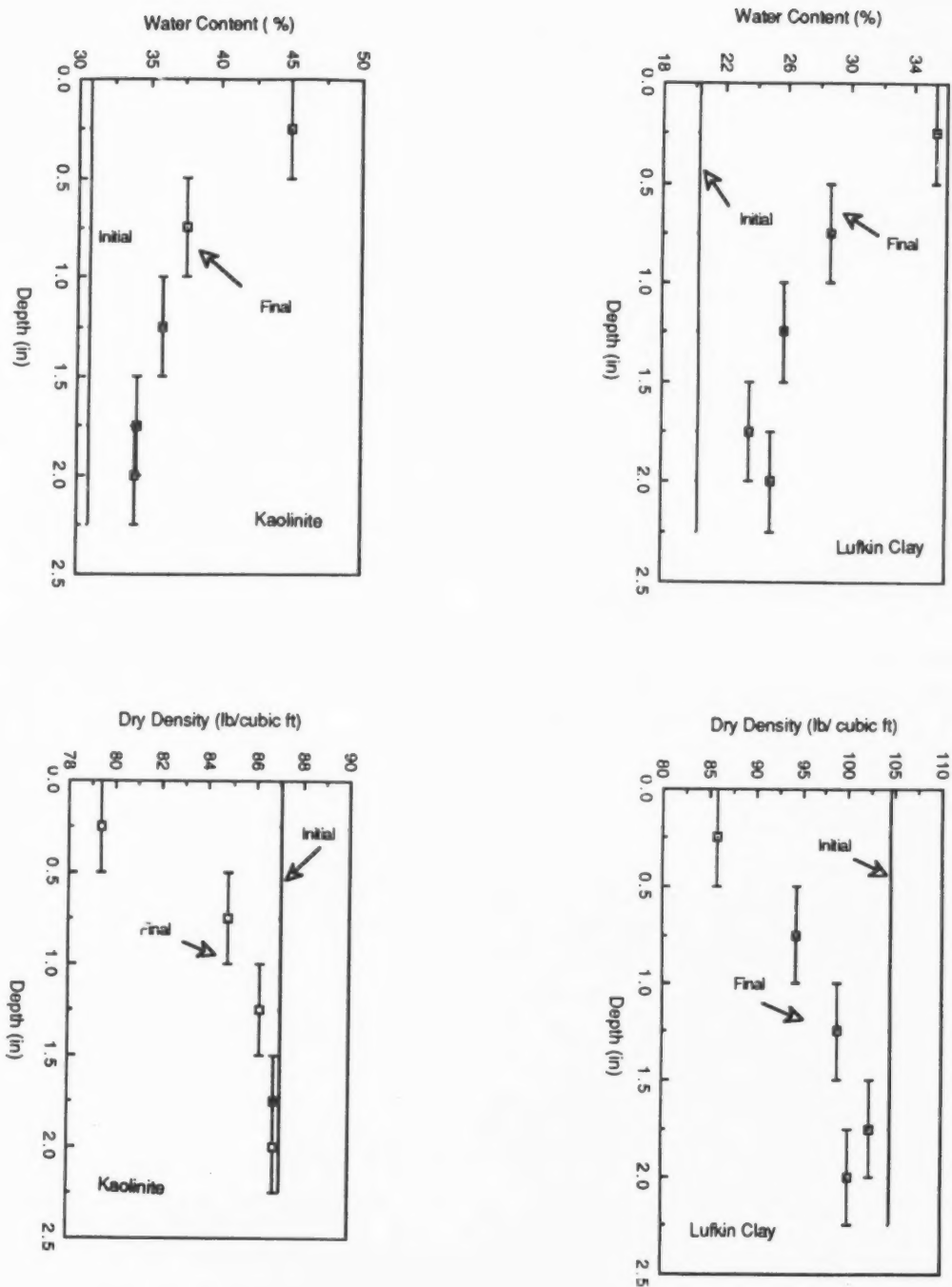


Figure 6.12 Typical Water Content and Density Profiles

The highest water content and lowest dry density were at the top of a specimen because swelling was not restrained at the top of the compacted specimens. The compacted clay samples swelled when given access to water. The kaolinite specimens swelled about 2.5 mm and the Lufkin clay swelled up to 10 mm. The vertical swelling percentages ranged from 2 to 5 for kaolinite and 5 to 20 for Lufkin clay.

Variations in water content and dry density may have led to variable hydraulic conductivity, diffusion coefficient, and other parameters that govern movement of solutes through the soil. These variations greatly complicate interpretation and analysis.

Temporal Variability -- Most of the presoaked columns showed a steady hydraulic conductivity over the testing period (a typical result is presented in Fig. 6.13). Rates of inflow and outflow were identical, except for columns with the lowest flow rates, for which, due to evaporative losses, outflow was slightly less than inflow. However, inflow and outflow rates differed by only a few percent.

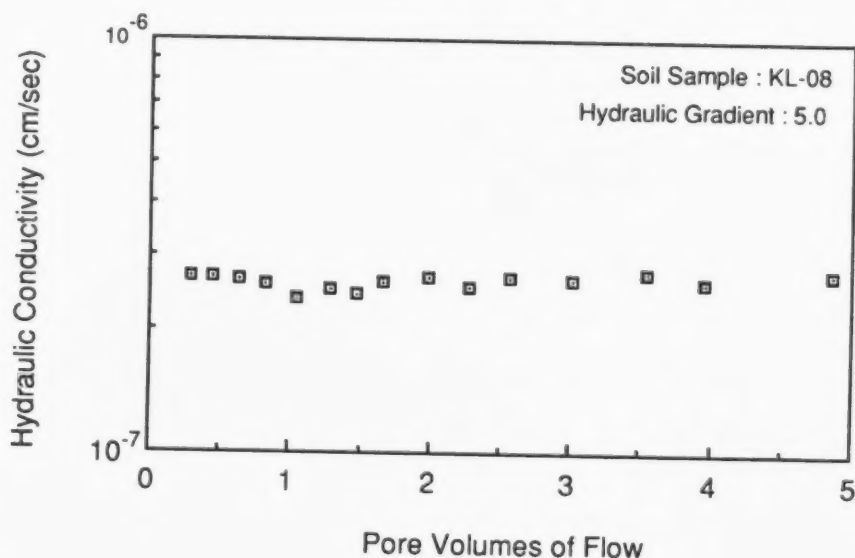


Figure 6.13 Typical Variation of Hydraulic Conductivity with Pore Volumes of Flow

Four kaolinite columns were checked for temporal stability by applying tracers at different times. No significant changes were noted over time, except for column KL-08, which was used for the checking of side-wall leakage before the second tracer was introduced. The soil specimen was disturbed during transfer between two different permeameters and this disturbance likely affected the results for subsequent tracers. One presoaked Lufkin clay column (LL-01) was also checked with two breakthrough curves. No noticeable change was observed in column LL-01.

All nonsoaked specimens swelled when the tracers were introduced into the soil columns. The soils underwent continuous changes in density as the water containing the tracers infiltrated into the soil columns. During this stage, inflow into the soil column was greater than than outflow.

Biological Environment

Changes in the chemical and biological conditions occurred in most of the soil columns during the testing period. Micro-organisms, e.g., bacteria, algae, and fungus, were evidently growing in the tracer solutions. Green algae were spotted on the top surface of two kaolinite columns. Sulfate bacteria existed in most of the soil columns; two soil columns were chemically affected by the precipitation of metal sulfides. In general, however, the effects of biological activity on the interpretation of tracer tests in this study was believed to be insignificant for reasons explained below.

Spots of green algae appeared on the top surface of two kaolinite columns (KL-15 and KL-17) a few weeks after the tracer solutions were introduced into the reservoir, then extended into a thin green film in the following months. After that, the growth stopped for several weeks, which was followed by a fading of the color into a pale green that remained through the entire test. The algae did not grow deeper than 1 mm into the soil column. Apparently, this system was biologically aerobic within the first few months. Then, either the available nutrients or dissolved oxygen was depleted, which minimized further algae growth.

There was one soil column (KL-04) that was particularly affected by sulfate bacteria. The solution in the reservoir was clear for the first few months until one day the water gradually became dark. Two weeks after the darkening began, a black substance sedimented on the soil surface, then the water became clear again. The odor of water indicated the presence of H_2S . The solution was sampled and analyzed. Neither potassium nor zinc had decreased in concentration; bromide and chloride were not depleted, either. But the sulfate content was decreased to a noticeably lower level.

The black precipitate was thought to be metal sulfides. The metal ions could have come from the brass fittings on the top of the reservoir or have been originally in the water. The odor indicated the existence of sulfide in the water, which was converted from sulfate by bacteria. The solution was soon replaced with a fresh solution to maintain the desired chemical conditions. In other soil

columns, the conversion of sulfate to sulfide was also believed to have occurred; in many column tests the sulfate concentration in the effluent was lower than the concentration in the influent reservoir.

The effect of biological growth with respect to hydraulic conductivity was insignificant; no significant changes in flow rate were observed. The reasons why biological growth did not affect hydraulic conductivity are believed to be:

1. The applied hydraulic gradient was not large enough to wash the microbial mass into the clay;
2. The small pore size within the clay soils caused a filtering of microbial mass and prevented significant penetration into the clay; a typical size for bacteria is 0.5-10 μm , and 2-100 μm for algae and fungi, while the average diameter of pore size in kaolinite is less than 0.1 μm and 0.5 μm in Lufkin; the "filter cake" or microbial matter apparently had a much higher hydraulic conductivity than the compacted clay; and
3. The supply of nutrients was too slow to cultivate a large amount of micro-organisms.

Griffin and Shimp (1978), Allison (1947), and Gupta and Swartzendruber (1962) have shown that microbial activities can reduce the hydraulic conductivity of porous media by clogging the voids in soil matrices. The materials that followed the trend were sandy soil or granular media used for filtering purposes. In the experiments of Griffin and Shimp, the soils that contained more than 32% clay did not behave like soils containing less clay, which underwent significant decreases in hydraulic conductivity with time.

A test was performed to examine the effect of microbial activities on the concentration of tracers. The test was conducted in a fixed-wall permeameter (same as the one used in the tracer tests) with the effluent outlet plugged. Two hundred grams of kaolinite were mixed with about 2000 ml of solution containing zinc, potassium, bromide, and chloride at the normal concentrations used in this study. A buret was used to monitor any evaporative loss. The reservoir was sampled periodically for 20 months, and the concentration of each tracer was measured. The changes in concentration of the tracers with time are shown in Figure 6.14. The effect of microbiological activities on bromide and chloride was insignificant. The concentrations of potassium and zinc dropped to about 80 percent of the initial concentration in the first few days and then remained relatively constant. The initial decrease of concentration of cations was likely due to sorption by the clay. There appeared to be no long-term loss of any of the tracers.

Results

The experimental data are presented in form of breakthrough curves. In this study, the most convenient form of presentation for a breakthrough curve was

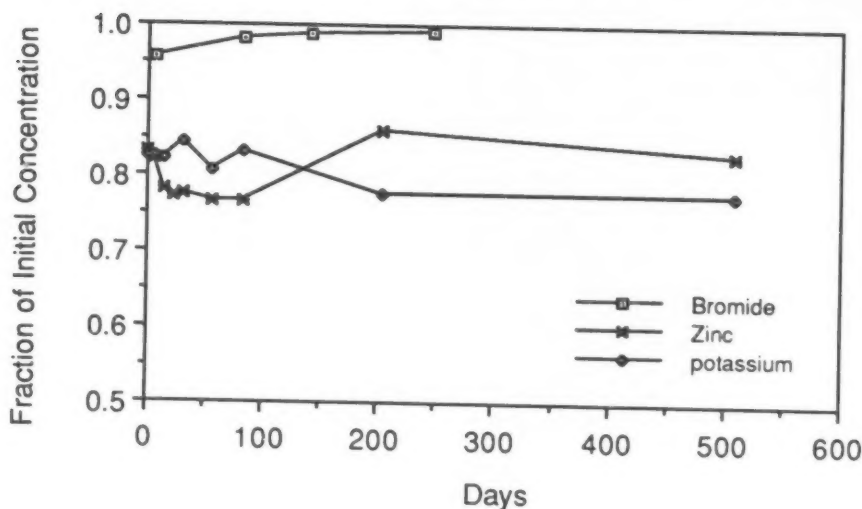


Figure 6.14 Long-Term Changes in Reservoir Concentration of Tracers

found to be a plot of the concentration (c) of a tracer in the effluent liquid, relative to the constant concentration (c_0) in the influent reservoir, or c/c_0 , versus pore volumes of flow. A pore volume of flow was determined by dividing the cumulative volume of inflow by the initial volume of the pore space within the test specimen.

The hydrodynamic dispersion coefficient, effective porosity ratio, and retardation factor were obtained by fitting an analytic solution (Ogata and Banks, 1961) to the experimental data as described in Section 5. The effective porosity ratio and hydrodynamic dispersion coefficient were varied until a best fit (by eye) was obtained. The computed effective porosity ratios from curve fitting were close (within about 20%) to the value of pore volumes of flow at $c/c_0 = 0.5$. Only if there were no molecular diffusion would one expect the curve-fitted value of n_e/n to equal exactly the number of pore volumes of flow at $c/c_0 = 0.5$. The curve-fitting procedure did not necessarily provide a unique solution for effective porosity ratio and hydrodynamic dispersion coefficient since two parameters were being varied during the fitting. However, varying the hydrodynamic dispersion coefficient mainly changed the slope of the breakthrough curve while varying the effective porosity ratio mainly translated the breakthrough curve.

Presoaked Kaolinite. Gradients of 10 and 20 -- Five breakthrough curves (3 adsorption curves and 2 desorption curves) were obtained from three soil columns (KL-02, KL-05, and KL-12). Typical breakthrough curves for bromide are presented in Figures 6.15 and 6.16. The points in the figures represent

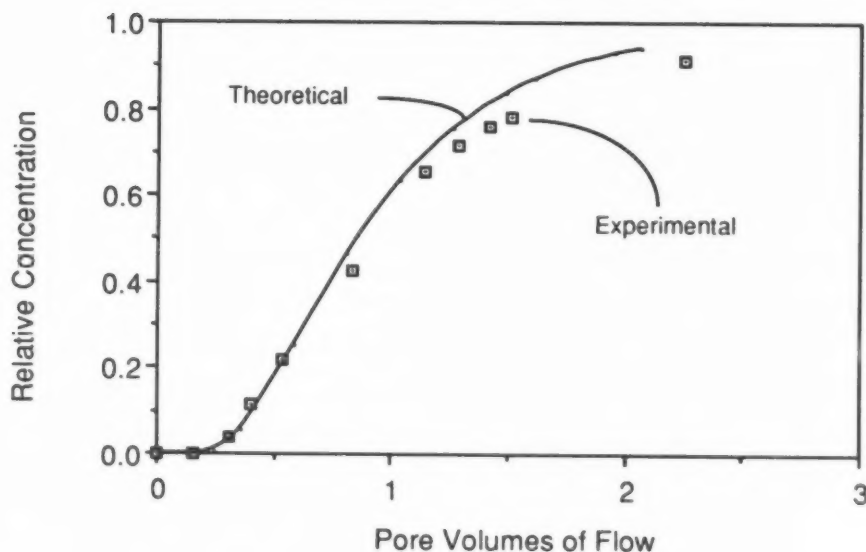


Figure 6.15 Breakthrough Curve for Bromide in Kaolinite Permeated at a Hydraulic Gradient of 20

experimental values, and the curve is the theoretically-calculated curve based on the values of hydraulic conductivity, hydraulic gradient, effective porosity ratio, and hydrodynamic dispersion coefficient summarized in Table 6.6. The effective porosity ratio is defined as the ratio between the effective porosity and the total porosity.

For columns KL-02 and KL-05, when all the tracers in the effluent reached the input concentration, the tracer solution was replaced with standard water. An "inverse breakthrough curve" or "desorption curve" was thus obtained. Both the breakthrough curve and inverse breakthrough curve obtained for bromide from KL-02 are shown in Figure 6.16. A good match exists between these two curves.

The calculated dispersion coefficient is $8 \times 10^{-6} \text{ cm}^2/\text{s}$ at a gradient of 10, and $1 \text{ to } 4 \times 10^{-5} \text{ cm}^2/\text{s}$ at a gradient of 20. At a gradient of 20, the hydrodynamic dispersion coefficients are significantly higher than the effective diffusion coefficient of bromide in kaolinite, which was $6 \text{ to } 7 \times 10^{-6} \text{ cm}^2/\text{s}$ (Table 6.4). At a gradient of 10, the hydrodynamic dispersion coefficient is approximately equal to the effective diffusion coefficient. The larger hydrodynamic dispersion

Table 6.6 Summary of Transport Properties for Bromide for Presoaked Kaolinite
Permeated at Gradients of 10 and 20

Soil Column	Hydraulic Conductivity cm/sec	Gradient	Dispersion Coefficient (cm ² /sec)	
			Breakthrough Curve	Inverse Breakthrough Curve
KL-02	2.7×10^{-7}	10	8×10^{-6}	8×10^{-6}
KL-05	3.6×10^{-7}	20	4×10^{-5}	2×10^{-5}
KL-12	2.3×10^{-7}	20	1×10^{-5}	NA

KL-02 and KL-05 were 5.58-inch-long columns.
KL-12 was a 2.29-inch-long column.

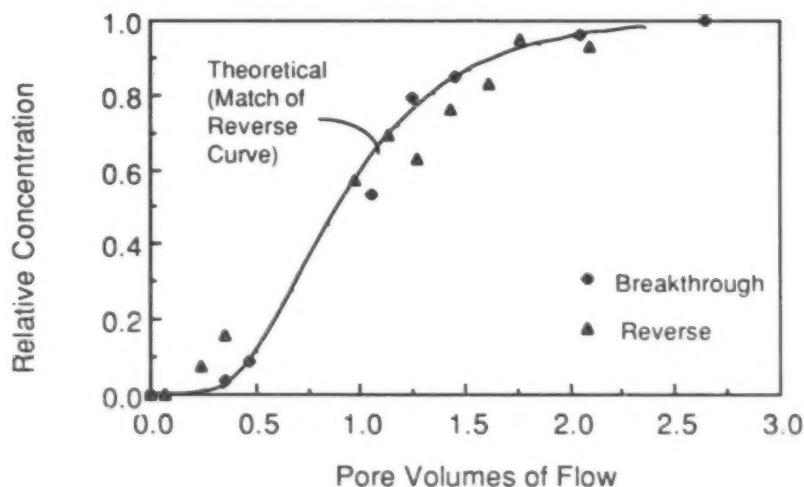


Figure 6.16 Breakthrough and Reverse Breakthrough Curves for Bromide Passing through Kaolinite at a Hydraulic Gradient of 10

coefficients at gradient of 20 are due to the higher flow velocity which caused more mechanical mixing.

Testing for column KL-05 was interrupted in the middle of the test due to clogging by a white precipitate in the effluent tube. The precipitate was not identified. The precipitate built up at the effluent end over a period of 2 months until essentially no outflow occurred. The permeameter was then disassembled to clean out the precipitate. The clogging occurred at pore volumes of flow between 1 and 2. The clogging occurred after breakthrough of the tracer and therefore had no influence on test results.

Two breakthrough curves for potassium (presented in Figure 6.17) at gradients of 10 and 20 were obtained from soil columns KL-02 and KL-05, respectively. The primary difference between the transport of potassium and bromide is the adsorption of potassium by the clay. The effective porosity ratio and hydrodynamic dispersion coefficient were assumed to be the same as the values computed from the results of breakthrough of bromide. To curve-fit the experimental data, the only unknown parameter (once the effective porosity ratio and hydrodynamic dispersion coefficient had been assumed) was the retardation

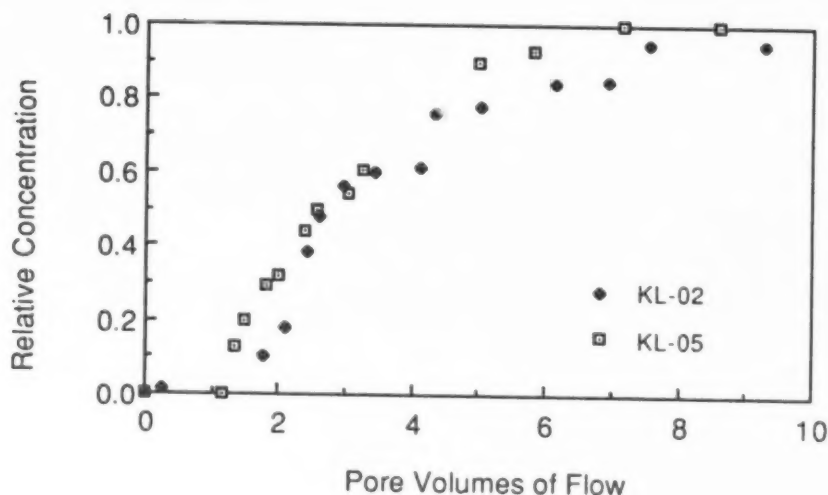


Figure 6.17 Breakthrough Curves for Potassium from Kaolinite Permeated at a Gradient of 10 and 20

factor. By trial-and-error curve fitting, the retardation factor for potassium was found to be 3.5 at gradient of 10 and of 3.0 at gradient of 20.

The retardation factor is often determined from the results of a batch adsorption test. Batch adsorption tests suggest retardation factors of 4.7 for column KL-02 and 4.5 for KL-05 (the difference is due to the different dry bulk densities of soil columns). The secant slope of the adsorption isotherm was used for the partition coefficient, K_d , in calculating retardation factors from batch adsorption tests. The comparison between retardation factors from the batch adsorption test and from the column tests indicates that the prediction from the batch adsorption test overestimates the retardation factor from column tests. Differences between column and batch tests are discussed later.

Presoaked Kaolinite. Gradient of 5 -- Two anions, bromide and chloride, were used as tracers. Since the results of bromide and chloride were identical, the results are given for bromide only. Breakthrough curves of bromide were obtained from five soil columns (KL-03, -08, -12, -15, and -17) at a concentration of 0.01 N. Another two were from KL-11 and KL-16 at a concentration of 0.001 N. A typical breakthrough curve for bromide is presented in Figure 6.18.

Two variables, the effective porosity ratio and hydrodynamic dispersion coefficient, were adjusted to curve-fit the experimental data as described earlier.

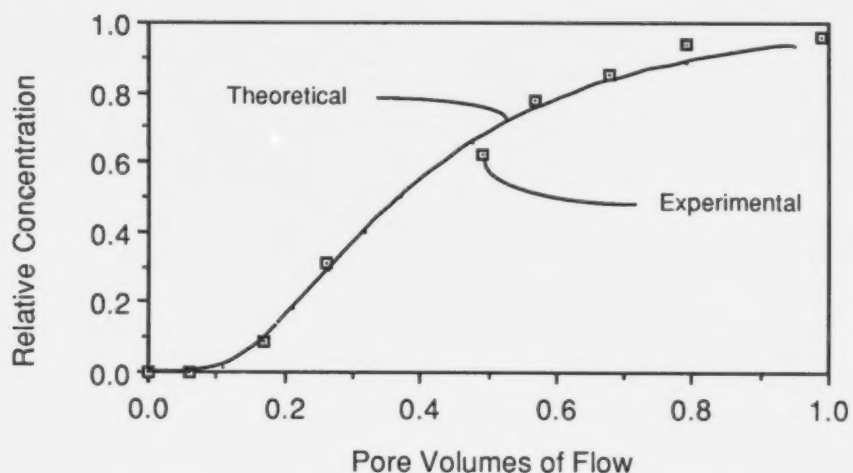


Figure 6.18 Breakthrough Curve for Bromide from Kaolinite Permeated at a Hydraulic Gradient of 5

The parameters computed from the trial-and-error curve fitting, along with other information concerning the columns, are listed in Table 6.7.

Four out of seven breakthrough curves had about the same effective porosity ratio (defined as effective porosity divided by total porosity, or n_e/n) of 0.54 -0.56. The sixth column (KL-03) had an effective porosity ratio of 0.85 and the seventh column (KL-12) had $n_e/n = 0.45$. The hydrodynamic dispersion coefficients are consistent throughout all seven tests. The value of hydrodynamic dispersion coefficient ranges from 4×10^{-6} to 6×10^{-6} cm²/s, which is approximately equal to the effective diffusion coefficient.

The two cationic tracers (zinc and potassium) were simultaneously introduced into the soil columns. Seven breakthrough curves, three for potassium and four for zinc, were obtained. The effective porosity values used in the calculation of transport parameters for zinc and potassium were from the results of accompanying anionic tracers. The dispersion coefficients were also obtained from anionic tracers with slight changes to better fit the experimental data. The retardation factors were obtained by trial and error curve fitting. The transport parameters are summarized in Table 6.8. The retardation factors were 3.5 and 3.2 for potassium at a concentration of 0.01 N (391 mg/L) and 4.0 for zinc at a concentration of 0.01 N (325 mg/L). The retardation factors for potassium are comparable to the retardation factors determined from columns tested at a hydraulic gradient of 20 in which no zinc competed for the adsorption sites on the

TABLE 6.7 Transport Properties for Bromide for Presoaked Kaolinite Columns
Tested at a Hydraulic Gradient of 5

Soil Column	Height of Column in.	Hydraulic Gradient	Hydraulic Conductivity cm/sec	Effective Porosity Ratio n_e/n	Hydrodynamic Dispersion Coefficient cm ² /sec
KL-03	4.58	5	1.7×10^{-7}	0.85	4×10^{-6}
KL-08	2.29	5	2.5×10^{-7}	0.56-0.80	6×10^{-6}
KL-12	2.29	5	1.7×10^{-7}	0.45	5×10^{-6}
KL-15	2.29	5	1.7×10^{-7}	0.54	6×10^{-6}
KL-17	4.58	5	8.3×10^{-8}	0.55	4×10^{-6}
KL-11	2.29	5	2.3×10^{-7}	0.54	6×10^{-6}
KL-16	2.29	5	2.0×10^{-7}	0.54	6×10^{-6}

TABLE 6.8 Retardation Factors for Potassium and Zinc from Column Tests
Performed at a Hydraulic Gradient of 5

Soil Column	Cation.	Hydraulic Gradient	Hydraulic Conductivity cm/sec	Effective Porosity Ratio	Hydrodynamic Dispersion Coefficient cm ² /sec	Retardation Factor
KL-03	K	5	1.7×10^{-7}	0.85	8×10^{-6}	3.5
KL-08	K	5	3.0×10^{-7}	0.80	1×10^{-5}	3.2
KL-08	Zn	5	3.0×10^{-7}	0.80	8×10^{-6}	4.0
KL-15	Zn	5	2.0×10^{-7}	---	---	---
KL-03	Zn	5	1×10^{-7}	---	---	---
KL-16*	K	5	2.0	0.54	2×10^{-5}	10
KL-16*	Zn	5	2.0	0.54	6×10^{-6}	11

* Note: Concentration of K and Zn in KL-16 is 0.001N, which is one tenth of the concentration in the rest of columns.

clay surfaces. At a lower concentration, 0.001N, the retardation factors increased to 10 for potassium and to 11 for zinc, which is due to the nonlinear isotherms in which the partition coefficient (K_d) is larger at a lower concentration.

The retardation factors computed from batch adsorption tests are summarized in Table 6.9 for presoaked kaolinite tested at a hydraulic gradient of 5. The batch tests predict: (1) a retardation factor of 3.44 for potassium and of 3.36 for zinc at a concentration of 0.01 N, which is comparable to the results of column tests; (2) a retardation factor of 6.27 for potassium and of 6.14 for zinc at the lower concentration (0.001 N), which is significantly lower than the results of column tests; and (3) that the attenuation of zinc should be less than the attenuation of potassium, which is opposite to the results of tracer column tests.

The effective porosity of column KL-08 was obtained from the inverse breakthrough curve for bromide, because the soil is believed to have been disturbed during the permeation test. The use of the effective porosity obtained from the initial breakthrough curve results in an unreasonably high value of dispersion coefficient.

The breakthrough curves for zinc from columns KL-03 and KL-15 are different from typical ones. There was a significant delay in zinc breakthrough from KL-03. The breakthrough occurred at 6.5 pore volumes of flow, which is about three and a half of pore volumes behind the expected breakthrough. The delay is attributed to the possible precipitation of zinc sulfide. Column KL-03 is one of the columns that had black sulfide in the reservoir in the early months of permeation. The effluent concentrations of zinc from columns of KL-03 and KL-15 never exceeded 70% of the influent concentration, even with up to seven pore volumes of flow. It was impossible to obtain a good fit between theoretical and experimental curves. Therefore, no values of dispersion coefficient and retardation factor are reported for zinc with columns KL-03 and KL-15.

Presoaked Kaolinite, Gradient of 1 -- Five breakthrough curves for anions were obtained from three soil columns (KL-09, KL-04, and KL-14). Chloride was introduced one year later than bromide, but otherwise there was no difference in the use of bromide compared to chloride. Figure 6.19 shows typical breakthrough curves for chloride and bromide. A good theoretical fit of the breakthrough data could not be achieved for bromide. The breakthrough curves for chloride are thought to be more reliable than the curves for bromide based on the more reasonable, and consistent, parameters computed from the chloride curves.

The values of effective porosity ratio and hydrodynamic dispersion coefficient determined from curve fitting are summarized in Table 6.10. A range of hydrodynamic dispersion coefficient is reported for some columns because precise fitting was not possible. The effective porosity ratios are generally in the range of 0.25 - 0.5. The hydrodynamic dispersion coefficients fall in the range of $4 - 6 \times 10^{-6} \text{ cm}^2/\text{s}$, which is approximately equal to the effective diffusion coefficient.

TABLE 6.9 Retardation Factors Based on Batch Adsorption
Tests for Soil Columns KL-03, KL-08 and KL-16

Soil Column	Competing		Dry Bulk		Retardation Factor $R_d = 1 + \frac{K_p \cdot \rho_b}{n}$
	Adsorbed Cation	Cation	Porosity	Density ρ_b (g/cm ³)	
KL-03	K	Zn, Ca	0.51	1.38	3.44
KL-08	K	Zn, Ca	0.51	1.39	3.45
KL-16	Zn	Zn, Ca	0.51	1.40	6.27
KL-08	Zn	K, Ca	0.51	1.39	3.36
KL-16	Zn	K, Ca	0.51	1.40	6.14

TABLE 6.10 Transport Coefficients in Kaolinite Tested at a Gradient of 1

Soil Column	Tracer	Height of Column in	Hydraulic Conductivity cm/sec	Effective Porosity Ratio	Hydrodynamic Dispersion Coefficient cm ² /sec
KL-01	Br	4.58	1.7x 10 ⁻⁷	- - -	- - -
KL-01	Cl	4.58	2.0x 10 ⁻⁷	0.25-0.50	(4 - 6) x 10 ⁻⁶
KL-04	Br	4.58	2.0x 10 ⁻⁷	0.9-1.0	4 x 10 ⁻⁶
KL-04	Cl	4.58	1.7x 10 ⁻⁷	0.25-0.50	(4 - 6) x 10 ⁻⁶
KL-14	Cl	2.29	3.0x 10 ⁻⁷	0.30-0.50	(4 - 6) x 10 ⁻⁶

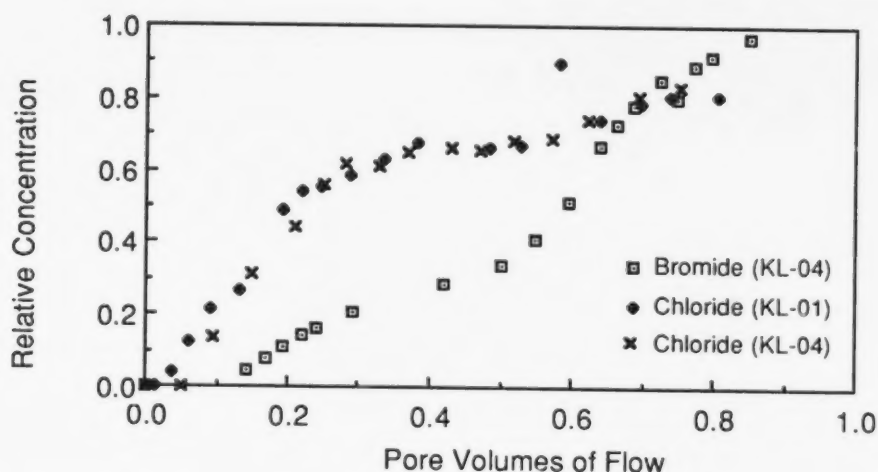


Figure 6.19 Breakthrough Curves for Anions from Kaolinite at a Gradient of 1

The breakthrough curve for chloride from column KL-14 leveled off at the relative concentration of 0.8 after 0.5 pore volumes of flow. The breakthrough curve for $c/c_0 < 0.7$ is fitted well with an effective porosity ratio of 0.3 and a hydrodynamic dispersion coefficient of $4 \times 10^{-6} \text{ cm}^2/\text{s}$.

Two breakthrough curves for potassium were obtained from two soil columns, KL-01 and KL-04, and are shown in Figure 6.20. Calculation of the retardation factor was complicated by the fact that the tests with anions failed to yield a precise value of effective porosity. Thus, in determining parameters from potassium breakthrough data, it was arbitrarily assumed that the retardation factor was 3.5, which is the approximate value of retardation factor obtained from tests at higher gradients.

The computed transport parameters for potassium are summarized in Table 6.11. The curve from column KL-04 can be fitted well with a hydrodynamic dispersion coefficient of $2 \times 10^{-6} \text{ cm}^2/\text{s}$ and an effective porosity ratio of 0.3. The curve from KL-01 could be fitted well by one set of parameters; ranges of parameters are reported in Table 6.11.

TABLE 6.11 Transport Properties of Nonsoaked Kaolinite Columns

Specimen Number	Height of Column in	Hydraulic Gradient	Hydraulic Conductivity cm/sec	Total Porosity	Effective Porosity Ratio	Hydrodynamic Dispersion Coefficient cm ² /sec	Tracer	Retardation Factor
KL-09	2.29	1.0	2.2×10^{-7}	0.48	0.2	0.4×10^{-5}	K	3.5
KL-09	2.29	1.0	3.17×10^{-7}	0.48	0.2	1.0×10^{-5}	Br	1.0
KL-14	2.29	1.0	2.5×10^{-7}	0.48	0.3	0.6×10^{-5}	K	3.5
KL-14	2.29	1.0	2.5×10^{-7}	0.48	0.2	1.0×10^{-5}	Br	1.0
KL-10	2.29	5.0	2.2×10^{-7}	0.48	1.0	1.2×10^{-5}	K	3.5
KL-10	2.29	5.0	2.0×10^{-7}	0.48	0.65	1.2×10^{-5}	Br	1.0
KL-15	2.29	5.0	1.8×10^{-7}	0.48	0.4	1.2×10^{-5}	K	3.5
KL-15	2.29	5.0	1.8×10^{-7}	0.48	0.3	1.5×10^{-5}	Br	1.0

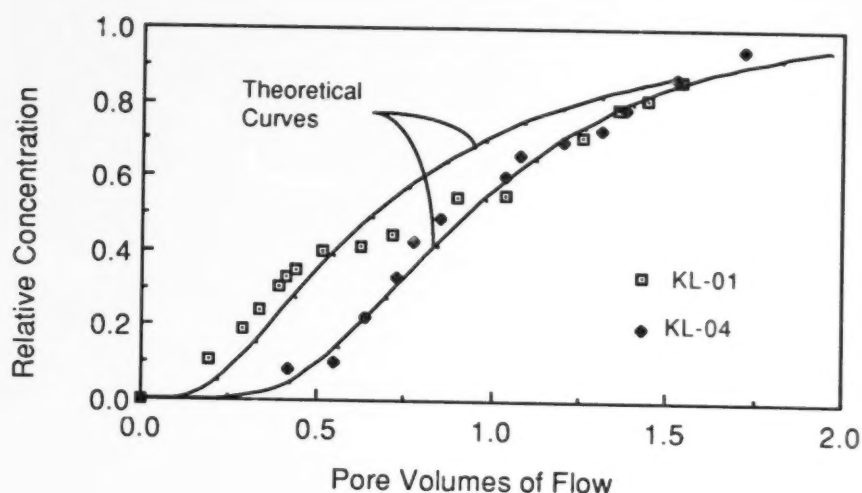


Figure 6.20 Breakthrough Curves for Potassium from Kaolinite Permeated at a Gradient of 1

The breakthrough curve for potassium from column KL-01 was irregular with a "hump" below 0.4 relative concentration (as shown in Figure 6.20). The lower part of the breakthrough curve could be fitted with an effective porosity ratio of 0.25; the upper part can be fitted with an effective porosity ratio of 0.3.

Nonsoaked Kaolinite -- Eight breakthrough curves from four columns of nonsoaked kaolinite permeated at two hydraulic gradients were obtained. For purposes of analysis, the volume of water in the soil columns was assumed to be the same as if the soils were saturated; since the degrees of saturation of these specimens ranged from 93% to 95% before the tracers were introduced, the assumption introduced little error. The data were analyzed both by the Ogata and Banks' solution and the computer program SOILINER (both are discussed in Section 5). Although the use of Ogata and Banks' solution is questionable for nonsoaked specimens, the analyses provided a common basis for comparisons with presoaked specimens.

The results of analyses with the Ogata and Banks solution, summarized in Table 6.11, indicate that the effective porosity ratio of a nonsoaked specimen was generally smaller than that of a presoaked specimen, while the dispersion coefficient was larger for a nonsoaked specimen. The effective porosity ratios of nonsoaked soils averaged 0.2 for specimens subjected to the gradient of 1.0. One specimen permeated at a gradient of 5 had an effective porosity ratio of 0.3 - 0.4, and the other 0.65 - 1.0. The dispersion coefficient for bromide was consistently

greater for nonsoaked soil than for soaked soil. The retardation factor of potassium was assumed to be 3.5 from the results of tests on presoaked specimens.

The results for column KL-10 were different from other columns. A review on the permeation data for column KL-10 reveals that, at the first stage when the tracers were introduced, inflow was already equal to outflow despite the fact that the column had not been presoaked. Other nonsoaked kaolinite specimens retained 10-20 ml liquid, which is the difference between total inflow and total outflow, within the first two weeks of testing.

The results of analyses with SOILINER are summarized in Table 6.12. The initial water contents and degrees of saturation for these columns were calculated from measurements obtained at the time of sample preparation. The initial suction head was estimated based on the assumed moisture characteristic curve (discussed in Section 5). The results consistently showed that breakthrough occurred earlier than predicted by SOILINER by a factor of up to 5 times. This indicated that SOILINER tends to overestimate the travel time for a nonreactive tracer. The overestimation of breakthrough time was most likely the result of the fact that effective porosity in kaolinite was less than the total porosity (SOILINER makes computations assuming that all the pores of the soil are equally effective in conducting flow).

Lufkin Clay -- Eight breakthrough curves for bromide were obtained from either presoaked or nonsoaked Lufkin clay columns permeated at gradients of 20 and 50. The transport properties, computed from curve fitting with the Ogata and Banks solution, are tabulated in Table 6.13. The hydraulic conductivities of the specimens ranged from 8.5×10^{-10} to 7.2×10^{-9} cm/s. The effective porosity ratios ranged from either 0.02 to 0.03, or from 0.12 to 0.16, without any number in between. The effect of presoaking the soil on effective porosity ratio was insignificant. Similarly, there is no relationship between effective porosity ratio and hydraulic gradient. The hydrodynamic dispersion coefficients fall in a narrow range of 8 to 10×10^{-6} cm²/s, which is also independent of soaking conditions or hydraulic gradient and is within the range of effective diffusion coefficients measured in diffusion tests.

No zinc and little potassium was detected in the effluent liquid over the testing period of up to 2 years. Sulfate appeared in most of the effluent liquids at a concentration less than the input concentration. Three Lufkin clay specimens were sectioned to determine concentration profiles of cationic tracers. Liquid samples from each reservoir were taken and analyzed for the cationic tracer. The concentration of zinc in the reservoir was only about 10% of the input concentration, and about 20% for potassium, when the soil columns were disassembled.

Typical concentration profiles of cationic tracers are presented in Figure 6.21. The potassium was uniformly distributed over the length of the soil column, while the concentration of zinc decreased with depth. More detailed analyses of the concentration profiles were not attempted.

TABLE 6.12 Comparisons Between the SOILINER Predictions and
Column Tests Results on Nonsoaked Kaolinite Columns

Column Number	Type of Soil	Hydraulic Gradient	Saturated Hydraulic Conductivity cm/sec	Initial Degree of Saturation %	Initial Pressure Head cm	Initial Water Content by Volume	Breakthrough Time	
							SOILINER Prediction (days)	Column Test Result (days)
KL-15	Kaolinite	5	1.8×10^{-7}	92.8	-20.0	0.437	31	8
KL-10	Kaolinite	5	2.0×10^{-7}	95.0	-15.1	0.449	28	13
KL-14	Kaolinite	1	2.5×10^{-7}	92.8	-20.0	0.437	62	17
KL-9	Kaolinite	1	3.1×10^{-7}	93.8	-16.9	0.480	84	16

TABLE 6.13 Transport Properties of Lufkin Clay Columns

Column Number	Height of Column in	Hydraulic Gradient	Hydraulic Conductivity cm/sec	Effective Porosity Ratio	Hydrodynamic Dispersion Coefficient cm ² /sec	Presoaked or Nonsoaked
LL-01	4.58	20	2.5 x 10 ⁻⁹	0.12	8 x 10 ⁻⁶	Presoaked
LL-12	2.29	20	1.2 x 10 ⁻⁹	0.03	1 x 10 ⁻⁵	Presoaked
LL-02	4.58	50	2.8 x 10 ⁻⁹	0.15	1 x 10 ⁻⁵	Presoaked
LL-11	2.29	50	1.7 x 10 ⁻⁹	0.12	1 x 10 ⁻⁵	Presoaked
LL-06	2.29	20	7.2 x 10 ⁻⁹	0.12	1 x 10 ⁻⁵	Nonsoaked
LL-13	2.29	20	1.5 x 10 ⁻⁹	0.02	1 x 10 ⁻⁵	Nonsoaked
LL-14	2.29	50	8.5 x 10 ⁻¹⁰	0.03	1 x 10 ⁻⁵	Nonsoaked
LL-05	2.29	50	3.1 x 10 ⁻⁹	0.16	8 x 10 ⁻⁶	Nonsoaked

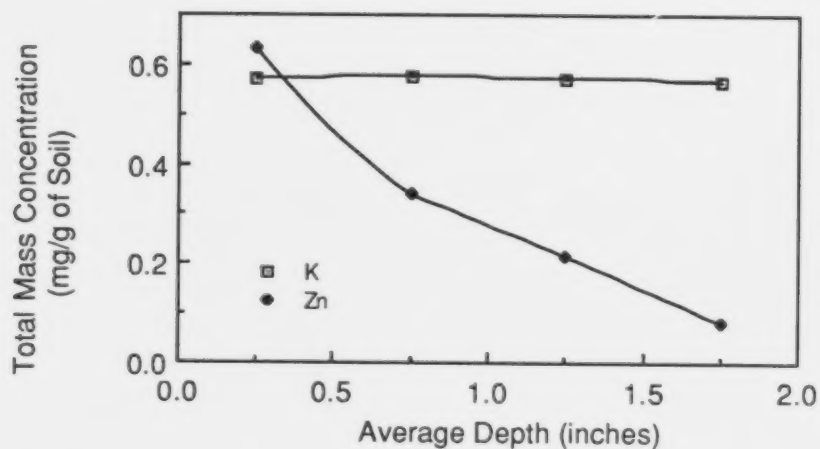


Figure 6.21 Typical Profiles of Tracers in Lufkin Clay Column at End of Permeation

Program SOILINER was used to analyze the results of tests on soil columns that were not soaked prior to introduction of tracers. Comparisons of predicted and actual breakthrough times are shown in Table 6.14. The computed breakthrough times were up to 52 times larger than the actual breakthrough times for anionic tracers. The reason why SOILINER overestimated breakthrough time are likely the same as discussed previously for kaolinite. The performance of SOILINER was worse for Lufkin clay than for kaolinite, probably because the effective porosity ratios for Lufkin clay were lower than for kaolinite, and effective porosity is assumed to equal total porosity in SOILINER.

To evaluate the effect of diffusional transport on the breakthrough curves, a diffusional transport index was defined as the ratio of the effective porosity to the pore volumes of flow at which breakthrough occurred. A larger diffusional transport index indicates that the influence of diffusional transport is more significant on the occurrence of breakthrough. The values of the transport index for kaolinite are listed in Table 6.15. The breakthrough curves for Lufkin clay were not adequately well defined to permit calculation of the diffusional transport index. The diffusional transport indices, ranging from 1.1 to 1.3 (Table 6.15), vary little with hydraulic gradient. The diffusional transport indices are only slightly greater than unity. The effective porosity ratios, in contrast, are much less than unity for most of the columns. Under the conditions of this study, the fact

TABLE 6.14 Comparisons Between SOILINER Predictions and Column Test Results
for Nonsoaked Lufkin Clay Columns

Column Number	Type of Soil	Hydraulic Gradient	Saturated Hydraulic Conductivity cm/sec	Initial Degree of Saturation %	Initial Pressure Head cm	Initial Water Content by Volume	SOILINER Prediction (days)	Breakthrough Time Column Test Result (days)
LL-5	Lufkin	50	3.1×10^{-9}	87.4	-37.0	0.332	162	19
LL-14	Lufkin	50	8.5×10^{-10}	89.3	-30.9	0.345	584	14
LL-6	Lufkin	20	7.2×10^{-9}	83.0	-52.5	0.325	195	16
LL-13	Lufkin	20	1.5×10^{-9}	92.1	-23.1	0.352	792	15

TABLE 6.15 Summary of the Transport Properties of Presoaked Kaolinite Columns

Column Number	Hydraulic Gradient	Hydraulic Conductivity cm/sec	Effective Porosity Ratio	Diffusional Transport Index cm/sec	Average Fluid Velocity	Hydrodynamic Dispersion Coefficient cm ² /sec
KL-12	20	2.25×10^{-7}	1.0	1.17	4.4×10^{-6}	10×10^{-6}
KL-05	20	3.60×10^{-7}	1.0	1.10	7.2×10^{-6}	$(20-40) \times 10^{-6}$
KL-02	10	2.70×10^{-7}	1.0	1.11	2.7×10^{-6}	8×10^{-6}
KL-06a	20	2.35×10^{-7}	1.0	1.18	4.7×10^{-6}	10×10^{-6}
KL-13a	20	3.60×10^{-7}	1.0	1.11	7.2×10^{-6}	10×10^{-6}
KL-03	5	1.7×10^{-7}	0.85	1.16	1.0×10^{-6}	4×10^{-6}
KL-08	5	2.5×10^{-7}	0.80	1.20	1.6×10^{-6}	6×10^{-6}

TABLE 6.15 Summary of the Transport Properties of
Presoaked Kaolinite Columns (continued)

Column Number	Hydraulic Gradient	Hydraulic Conductivity cm/sec	Effective Porosity Ratio	Diffusional Transport Index cm/sec	Average Fluid Velocity	Hydrodynamic Dispersion Coefficient cm ² /sec
KL-12	5	1.7×10^{-7}	0.45	1.21	1.9×10^{-6}	5×10^{-6}
KL-15	5	1.7×10^{-7}	0.54	1.30	1.6×10^{-6}	6×10^{-6}
KL-11	5	2.3×10^{-7}	0.54	1.22	2.1×10^{-6}	6×10^{-6}
KL-16	5	2.0×10^{-7}	0.54	1.26	1.9×10^{-6}	6×10^{-6}
KL-01	1	1.7×10^{-7}	0.25-0.30 ^a	1.12	0.67×10^{-6}	$(4-6) \times 10^{-6}$
KL-04	1	2.0×10^{-7}	0.3 ^a	1.12	0.67×10^{-6}	$(4-6) \times 10^{-6}$

^a Data are from cationic tracers.

that the effective porosity ratio was significantly less than 1 had much more impact on breakthrough than did molecular diffusion.

Influence of Presoaking

There were two major differences in the breakthrough curves associated with presoaked and nonsoaked kaolinite specimens: a lower effective porosity ratio and a higher dispersion coefficient were observed for nonsoaked specimens. The data are compared in Table 6.16.

More gas is expected in a nonsoaked specimen than in a presoaked specimen. Differences in transport properties between nonsoaked and presoaked specimens would be expected based on differing volumes of gas. The fact that more of the pore space was filled with gas in the nonsoaked soils accounts for lower effective porosity in unsoaked soils. The cause for greater mechanical dispersion in the unsoaked soils is not readily apparent, but more tortuous flow paths in the nonsoaked soils would provide a logical explanation.

The effect of presoaking was not significant on the breakthrough curves for Lufkin clay specimens. The soaking period of one month was probably not long enough to eliminate entirely the capillary interface between the gas phase and the liquid phase. During the soaking period, no outflow emerged from the specimens. Thus, the soaking did not significantly affect the breakthrough curves.

COLUMN TESTS VERSUS BATCH TESTS TO DETERMINE RETARDATION FACTORS

The retardation factors based on the results of batch adsorption tests and column tests are summarized in Table 6.17. The retardation factors estimated from batch adsorption tests tended to overestimate the retardation capability of kaolinite for potassium at a concentration of 0.01N (391 mg/L), and tended to underestimate the retardation factors for zinc.

The overestimation of the retardation factor could be partly attributed to the hydrodynamic differences between a batch system and a soil column. In a batch test, the solute is shaken with soil to assure free contact with all the possible adsorption sites on the surfaces of clay particles, which is not the case in column tests where soil particles are not free to move around. The low effective porosities measured in this study suggest that in soil columns, the solutes are not exposed equally well to the surfaces of all the soil particles.

Differences between chemical environments in batch tests and column tests are also expected. The background cation species adsorbed on the surfaces of clay particles remain in the batch system to compete for exchange sites, while, in column tests, the desorbed background cations are flushed out of the system. The chemical properties of pore water in a soil column will eventually be the same as those of the influent liquid.

TABLE 6.16 Comparison of Transport Properties Between Nonsoaked
and Presoaked Kaolinite Columns

Nonsoaked Soil Column	Hydraulic Gradient	Effective Porosity Ratio	Hydrodynamic Dispersion Coefficient cm ² /sec	Presoaked Soil Column	Hydraulic Gradient	Effective Porosity Ratio	Hydrodynamic Dispersion Coefficient cm ² /sec
KL-09	1.0	0.20	1x10 ⁻⁵	KL-01	1.0	0.25-0.50	(4-6)x10 ⁻⁶
KL-14	1.0	0.20	1x10 ⁻⁵	KL-04	1.0	0.25-0.50	(4-6)x10 ⁻⁶
KL-15	5.0	0.30	1.5x10 ⁻⁵	KL-15	5.0	0.54	6x10 ⁻⁶
KL-17	5.0	0.45	1.2x10 ⁻⁵	KL-12	5.0	0.45	5x10 ⁻⁶
KL-18	1.0	0.20	1.2x10 ⁻⁵				

TABLE 6.17 Comparison Between Retardation Factors Obtained from Column Tests
and from Batch Adsorption Tests

Soil Column	Adsorbed Cation	Competing Cation	Retardation		Batch Test
			Column Test	Factor	
KL-02	K	Ca	3.5		4.66
KL-05	K	Ca	3.0		4.45
KL-03	K	Zn,Ca	3.5		3.44
KL-08	K	Zn,Ca	3.2		3.45
KL-08	Zn	K, Ca	4.0		3.36
KL-16*	K	Zn, Ca	10.0		6.27
KL-16*	Zn	K, Ca	11.0		6.14

* The influent concentration was 0.001N.

Another cause for the difference in chemical environments between batch tests and column tests is that the cations migrate at different velocities. The slower species (Zn) compete with the more mobile species (K) of higher concentration on particle surfaces. On the other hand, in the batch tests, competing species are added at the same concentration to the soil/water mixture, resulting in an equilibrium condition between species which rarely matches the condition in the column test. Control over the equilibrium concentration of each species in a batch test can only be achieved by trial and error, which is a time consuming process.

Batch adsorption tests with Zn and K competing for exchange sites predict a slightly higher retardation factor for potassium than that for zinc (3.45 for K versus 3.36 for Zn). However, column tests showed an opposite order; the retardation factor was 4.0 for zinc and 3.2 for potassium. The conflicting results are believed to be associated with the approximately same affinity of both species to kaolinite.

EFFECT OF HYDRAULIC GRADIENT ON TRANSPORT PROPERTIES

Little effect of hydraulic gradient was seen with Lufkin clay. With kaolinite, substantial differences in effective porosity were observed as a function of the hydraulic gradient used in a column test. The effective porosity ratio (n/n_e) from breakthrough of anionic tracers in kaolinite columns is plotted as a function of hydraulic gradient in Figure 6.22. A trend of increasing n/n_e with increasing hydraulic gradient is evident.

The low effective porosity ratios in kaolinite at hydraulic gradients of 1 and 5 is thought to be associated with viscous water adsorbed on clay surfaces. Low (1976) showed that the viscosity of water in a Na-montmorillonite system is related exponentially to the reciprocal of the water content by weight. The basic data used for the calculation of water viscosities in montmorillonite-water systems were obtained from experiments on viscous flow of water at different temperatures, self-diffusion of water, and neutron scattering by water. Low attributed the elevated viscosity of water in a montmorillonite-water system to visco-electric effects, the influence of exchangeable cations, and the effect of charged clay particles. The same effects may exist in other clay systems, as well.

Based on the scenario of elevated viscosity of water near the surfaces of clay particles, it is postulated that water in the central part of flow channels moved freely in accord with the hydraulic gradient applied to it and that the water in small pores was too viscous to flow and remained stagnant, except at higher hydraulic gradients. As the hydraulic gradient was decreased, it is speculated that viscous, adsorbed water became less mobile and served to block some flow paths rather than to conduct flow of water.

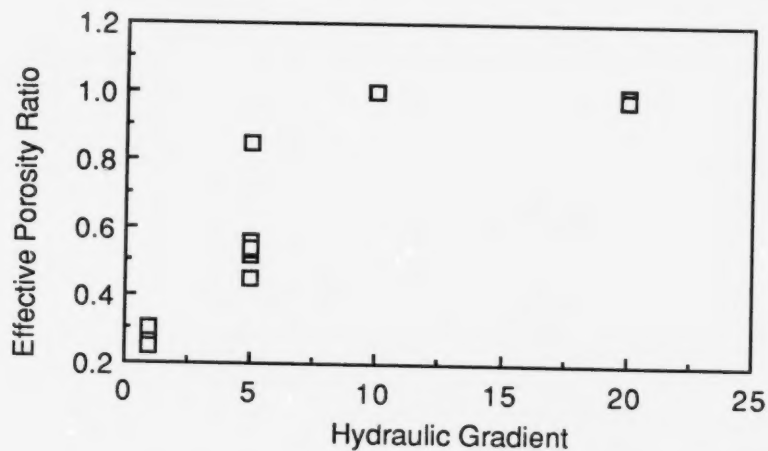


Figure 6.22 Effective Porosity Ratio Versus Hydraulic Gradient for Kaolinite

If viscous water served to influence effective porosity ratio, then it is logical to expect that viscous water would also influence the flow rate. The relationship between flux (defined as the rate of flow per unit area) and hydraulic gradient is shown in Figure 6.23 for kaolinite columns. The slope of this plot is the hydraulic conductivity of the soil. There is a trend for proportionally lower fluxes at lower hydraulic gradient, which is consistent with the postulation concerning viscous water presented previously. However, there was no hydraulic gradient at which the flux was zero, i.e., there was no evidence of the existence of a threshold hydraulic gradient.

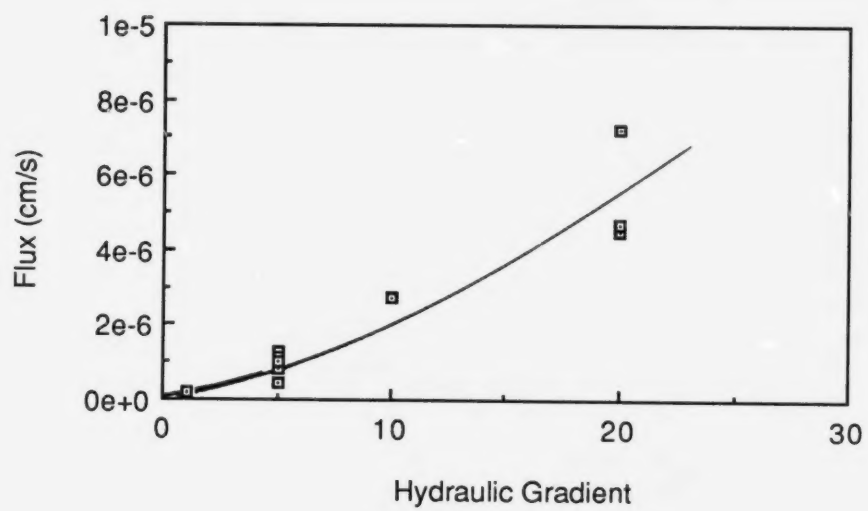


Figure 6.23 Flux Versus Hydraulic Gradient for Kaolinite

SECTION 7

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APPENDIX

DATA FROM COLUMN TESTS

COLUMN NO: KL-01					
TYPE OF SOIL: KAOLINITE					
HYDRAULIC GRADIENT: 1					
PORE VOLUME	RELATIVE CONCENTRATION (CHLORIDE)	PORE VOLUME	RELATIVE CONCENTRATION (BROMIDE)	PORE VOLUME	RELATIVE CONCENTRATION (POTASSIUM)
0.00	0.00	0.00	0.00	0.00	0.00
0.05	0.00	0.02	0.13	0.19	0.11
0.10	0.14	0.05	0.38	0.29	0.19
0.15	0.31	0.08	0.62	0.34	0.24
0.21	0.44	0.10	0.69	0.39	0.30
0.25	0.56	0.12	0.63	0.41	0.33
0.28	0.62	0.14	0.59	0.44	0.35
0.33	0.61	0.16	0.50	0.51	0.40
0.37	0.65	0.18	0.78	0.62	0.41
0.43	0.66	0.19	0.53	0.72	0.44
0.47	0.66	0.25	0.36	0.90	0.55
0.52	0.68	0.32	0.29	1.04	0.55
0.57	0.69	0.39	0.30	1.26	0.71
0.62	0.74	0.32	0.33	1.36	0.79
0.69	0.80	0.49	0.39	1.44	0.81
0.75	0.83	0.58	0.69	1.54	0.86
		0.62	0.77		
		0.67	0.84		
		0.72	0.91		
		0.77	0.94		

COLUMN NO: KL-02			
TYPE OF SOIL: KAOLINITE			
HYDRAULIC GRADIENT: 10			
PORE VOLUME	RELATIVE CONCENTRATION (BROMIDE)	PORE VOLUME	RELATIVE CONCENTRATION (POTASSIUM)
0.00	0.00	0.00	0.00
0.07	0.00	0.24	0.01
0.24	0.07	1.76	0.10
0.35	0.16	2.10	0.18
0.97	0.57	2.27	0.22
1.13	0.69	2.41	0.38
1.27	0.63	2.60	0.48
1.43	0.76	2.95	0.56
1.61	0.83	3.43	0.60
1.76	0.95	4.10	0.61
2.10	0.93	4.33	0.76
9.28	1.00	5.03	0.78
9.70	0.96	6.13	0.84
9.82	0.91	6.92	0.85
10.40	0.47	7.55	0.95
10.60	0.21	9.28	0.95
11.00	0.09	10.40	0.74
11.40	0.04	10.60	0.59
12.00	0.00	11.00	0.61
		11.40	0.53
		12.40	0.44
		13.20	0.39
		13.70	0.35
		14.80	0.29
		15.80	0.21
		16.90	0.17

COLUMN NO: KL-03									
TYPE OF SOIL: KAOLINITE									
HYDRAULIC GRADIENT: 5									
PORE VOLUME (ANIONS)	RELATIVE CONCENTRATION (BROMIDE)	RELATIVE CONCENTRATION (CHLORIDE)	PORE VOLUME (POTASSIUM)	RELATIVE CONCENTRATION (POTASSIUM)	PORE VOLUME (ZINC)	RELATIVE CONCENTRATION (ZINC)			
0.00	0.00	0.00	0.00	0.00	0.00	0.00			
0.20	0.06	0.03	0.46	0.07	4.98	0.00			
0.31	0.10	0.07	1.06	0.13	5.31	0.14			
0.37	0.16	0.11	1.40	0.26	5.62	0.24			
0.46	0.25	0.20	1.57	0.32	6.13	0.42			
0.62	0.38	0.32	1.71	0.37	6.50	0.52			
0.72	0.49	0.43	2.00	0.45	6.96	0.60			
0.85	0.54	0.50	2.28	0.51	7.45	0.66			
0.93	0.66	0.59	2.81	0.59	7.86	0.71			
1.06	0.75	0.65	3.69	0.72					
1.21	0.84	0.72	4.29	0.80					
1.40	0.92	0.79	4.98	0.84					
1.57	0.93	0.81	6.13	0.91					
1.83	0.97	0.84	7.86	0.91					
2.13	0.99	0.85							

COLUMN NO: KL-04					
TYPE OF SOIL: KAOLINITE					
HYDRAULIC GRADIENT: 1					
PORE VOLUME (BROMIDE)	RELATIVE CONCENTRATION	PORE VOLUME (CHLORIDE)	RELATIVE CONCENTRATION	PORE VOLUME (POTASSIUM)	RELATIVE CONCENTRATION
0.00	0.00	0.00	0.00	0.00	0.00
0.14	0.04	0.01	0.00	0.42	0.08
0.17	0.08	0.04	0.04	0.55	0.10
0.19	0.11	0.06	0.13	0.64	0.22
0.22	0.14	0.09	0.22	0.73	0.33
0.24	0.16	0.13	0.27	0.77	0.43
0.29	0.21	0.19	0.48	0.85	0.49
0.42	0.29	0.22	0.54	1.04	0.60
0.50	0.34	0.25	0.55	1.08	0.66
0.55	0.41	0.29	0.58	1.20	0.70
0.60	0.51	0.34	0.63	1.31	0.73
0.64	0.67	0.38	0.68	1.38	0.78
0.66	0.73	0.48	0.66	1.53	0.87
0.69	0.78	0.53	0.67	1.72	0.95
0.73	0.85	0.58	0.90		
0.75	0.80	0.64	0.74		
0.77	0.89	0.70	0.79		
0.80	0.92	0.74	0.80		
0.85	0.97	0.81	0.80		
		0.77	0.94		

COLUMN NO: KL-05			
TYPE OF SOIL: KAOLINITE			
HYDRAULIC GRADIENT: 20			
PORE VOLUME (BROMIDE)	RELATIVE CONCENTRATION	PORE VOLUME (POTASSIUM)	RELATIVE CONCENTRATION
0.00	0.00	0.00	0.00
0.08	0.07	1.15	0.00
0.27	0.07	1.32	0.13
0.37	0.13	1.49	0.20
0.57	0.20	1.80	0.29
0.77	0.40	2.00	0.32
0.97	0.52	2.40	0.44
1.07	0.61	2.58	0.50
1.15	0.62	3.02	0.54
1.24	0.64	3.24	0.61
1.32	0.76	5.00	0.90
1.43	0.71	5.81	0.93
1.63	0.70	7.14	1.00
1.93	0.79	8.61	1.00
2.40	0.94	10.34	1.00
10.34	1.00	11.40	0.87
10.80	0.98	11.80	0.70
10.95	0.84	12.40	0.52
11.22	0.65	13.10	0.51
11.40	0.45	13.70	0.49
11.70	0.29	14.70	0.38
11.80	0.19	15.60	0.33
12.10	0.11	16.40	0.29
12.40	0.06	16.60	0.26
13.10	0.00	17.60	0.19
		18.40	0.17
		19.30	0.14
		19.80	0.10
		21.80	0.05

COLUMN NO: KL-08					
TYPE OF SOIL: KAOLINITE					
HYDRAULIC GRADIENT: 5					
PORE VOLUME (ANIONS)	RELATIVE CONCENTRATION (BROMIDE)	RELATIVE CONCENTRATION (CHLORIDE)	PORE VOLUME (CATIONS)	RELATIVE CONCENTRATION (ZINC)	RELATIVE CONCENTRATION (POTASSIUM)
0.00	0.00	0.00	0.00	0.00	0.00
0.29	0.25	0.24	0.83	0.02	0.11
0.44	0.41	0.36	1.05	0.10	0.26
0.64	0.68	0.63	1.29	0.19	0.35
0.83	0.78	0.72	1.47	0.26	0.38
1.05	0.87	0.78	1.67	0.33	0.49
1.29	0.91	0.83	1.98	0.42	0.55
1.47	0.94	0.85	2.57	0.54	0.70
1.67	0.94	0.86	3.01	0.61	0.73
4.26	0.97	0.89	3.54	0.68	
12.02	0.98	0.92	3.96		0.81
13.71	0.83	0.81	4.50	0.75	0.78
13.83	0.69	0.69	4.86	0.81	0.85
13.88	0.46	0.58	5.30	0.78	0.84
14.00	0.42	0.40	7.33	0.82	0.86
14.11	0.34	0.37	9.83		0.93
14.22	0.27	0.29	11.40		0.97
14.43	0.21	0.22	12.00	0.91	0.92
14.56	0.14	0.19	13.33	1.00	1.00
14.66	0.15	0.15	13.71	0.80	0.81
			13.88	0.61	0.70
			14.22	0.47	0.56
			14.56	0.41	0.49
			14.84		0.40
			15.24		0.37
			15.57	0.37	0.33
			16.52	0.32	0.30
			17.58	0.29	0.28
			20.20	0.22	0.22
			23.19	0.16	0.14

COLUMN NO: KL-09 (NONSOAKED)					
TYPE OF SOIL: KAOLINITE					
HYDRAULIC GRADIENT: 1					
PORE VOLUME (ANIONS)	RELATIVE CONCENTRATION (BROMIDE)	RELATIVE CONCENTRATION (CHLORIDE)	PORE VOLUME (CATIONS)	RELATIVE CONCENTRATION (ZINC)	RELATIVE CONCENTRATION (POTASSIUM)
0.00	0.00	0.00	0.00	0.00	0.00
0.05	0.17	0.18	0.26	0.04	0.12
0.14	0.58	0.53	0.34	0.08	0.24
0.26	0.73	0.68	0.39	0.20	0.30
0.39	0.87	0.79	0.44	0.29	0.37
0.48	0.93	0.87	0.48	0.31	0.46
0.82	0.98	0.89	0.53	0.34	0.48
2.81	0.99	0.94	0.58	0.45	0.57
2.99	0.96	0.92	0.69	0.49	0.64
3.03	0.85	0.83	0.78	0.53	0.69
3.09	0.74	0.72	1.04	0.57	0.78
3.13	0.60	0.60	1.14	0.66	0.81
3.19	0.52	0.50	1.82	0.70	0.82
3.27	0.39	0.40	1.97	0.72	0.83
3.34	0.26	0.31	2.27	0.83	0.86
3.40	0.26	0.25	2.41	0.86	0.86
3.45	0.21	0.20	2.81	0.88	0.84
			2.99	0.85	0.83
			3.03		0.83
			3.09	0.73	0.76
			3.13		0.67
			3.19		
			3.27	0.60	0.57
			3.34	0.42	0.51
			3.40	0.39	0.50
			3.45	0.36	0.47
			3.63	0.29	0.35
			3.83	0.27	0.28
			4.00	0.26	0.25

COLUMN NO: KL-11		
TYPE OF SOIL: KAOLINITE		
HYDRAULIC GRADIENT: 5		
PORE VOLUME (ANIONS)	RELATIVE CONCENTRATION (BROMIDE)	RELATIVE CONCENTRATION (CHLORIDE)
0.00	0.00	0.00
0.09	0.08	0.12
0.31	0.16	0.21
0.47	0.61	0.54
0.52	0.65	0.60
0.79	0.81	0.76
0.96	0.91	0.81
1.14	0.94	0.84

COLUMN NO: KL-12			
TYPE OF SOIL: KAOLINITE			
HYDRAULIC GRADIENT: 5 (BROMIDE) AND 20 (CHLORIDE)			
PORE	RELATIVE	PORE	RELATIVE
VOLUME	CONCENTRATION	VOLUME	CONCENTRATION
(BROMIDE)		(CHLORIDE)	
0.00	0.00	0.00	0.00
0.06	0.00	0.15	0.00
0.17	0.09	0.31	0.04
0.26	0.31	0.40	0.12
0.49	0.62	0.54	0.22
0.57	0.78	0.84	0.43
0.68	0.85	0.94	
0.79	0.94	1.14	0.66
0.99	0.96	1.28	0.71
		1.42	0.76
		1.52	0.78
		2.25	0.91

COLUMN NO: KL-14					
TYPE OF SOIL: KAOLINITE					
HYDRAULIC GRADIENT: 1					
PORE VOLUME (NONSOAKED)	RELATIVE CONCENTRATION (BROMIDE)	PORE VOLUME (PRESOAKED)	RELATIVE CONCENTRATION (CHLORIDE)	PORE VOLUME (NONSOAKED)	RELATIVE CONCENTRATION (POTASSIUM)
0.00	0.00	0.00	0.00	0.00	0.00
0.06	0.16	0.05	0.04	0.21	0.08
0.10	0.44	0.10	0.15	0.31	0.28
0.16	0.60	0.15	0.33	0.41	0.35
0.21	0.70	0.20	0.45	0.60	0.43
0.26	0.78	0.25	0.55	0.80	0.47
0.36	0.86	0.30	0.63	0.89	0.53
0.52	0.88	0.35	0.67	1.04	0.70
		0.41	0.73	1.15	0.77
		0.46	0.75	1.25	0.84
		0.51	0.74	1.35	0.84
		0.55	0.77	1.50	0.87
		0.81	0.78	1.96	0.87
		1.10	0.79	2.44	0.87
				2.80	0.91

COLUMN NO: KL-16							
TYPE OF SOIL: KAOLINITE							
HYDRAULIC GRADIENT: 5							
PORE VOLUME (ANIONS)	RELATIVE CONCENTRATION (BROMIDE)	RELATIVE CONCENTRATION (CHLORIDE)	PORE VOLUME (CATIONS)	RELATIVE CONCENTRATION (ZINC)	RELATIVE CONCENTRATION (POTASSIUM)		
0.00	0.00	0.00	0.00	0.00	0.00		
0.10	0.17	0.26	0.91	0.03	0.17		
0.24	0.34	0.41	1.20	0.06	0.24		
0.33	0.46	0.50	1.63	0.12	0.30		
0.46	0.62	0.65	2.37	0.24	0.39		
0.67	0.71	0.72	2.74	0.22	0.45		
0.77	0.78	0.78	3.19	0.26	0.47		
0.91	0.83	0.82	3.62	0.35	0.49		
1.06	0.88	0.86	4.04	0.43	0.54		
1.41	0.90	0.89	4.34	0.46	0.52		
2.03	0.97	0.94	4.76	0.50	0.68		
			5.12	0.57	0.72		
			5.49	0.59	0.68		

COLUMN NO: KL-17			
TYPE OF SOIL: KAOLINITE			
HYDRAULIC GRADIENT: 5			
PORE VOLUME (NONSOAKED)	RELATIVE CONCENTRATION (BROMIDE)	PORE VOLUME (PRESOAKED)	RELATIVE CONCENTRATION (CHLORIDE)
0.00	0.00	0.00	0.00
0.08	0.05	0.16	0.07
0.11	0.11	0.20	0.16
0.16	0.26	0.32	0.31
0.22	0.38	0.39	0.39
0.27	0.45	0.40	0.45
0.31	0.50	0.41	0.49
0.35	0.54		
0.39	0.58		
0.43	0.60		
0.60	0.68		
0.70	0.73		
0.76	0.78		
0.87	0.82		
1.03	0.87		
1.09	0.90		

COLUMN NO: LL-01			COLUMN NO: LL-02			COLUMN NO: LL-05		
TYPE OF SOIL: LUFKIN			TYPE OF SOIL: LUFKIN			TYPE OF SOIL: LUFKIN		
HYDRAULIC GRADIENT: 20			HYDRAULIC GRADIENT: 50			HYDRAULIC GRADIENT: 50		
PORE VOLUME	RELATIVE CONCENTRATION (BROMIDE)	PORE VOLUME	RELATIVE CONCENTRATION (BROMIDE)	PORE VOLUME	RELATIVE CONCENTRATION (BROMIDE)	PORE VOLUME (NONSOAKED)	RELATIVE CONCENTRATION (BROMIDE)	
0.00	0.00	0.03	0.00	0.03	0.00	0.04	0.69	
0.04	0.10	0.07	0.00	0.07	0.00	0.10	0.67	
0.08	0.50	0.11	0.55	0.11	0.55	0.18	0.70	
0.11	0.63	0.15	0.68	0.15	0.68	0.29	0.85	
0.15	0.73	0.21	0.78	0.21	0.78	0.38	0.92	
0.19	0.83	0.25	0.82	0.25	0.82	0.51	0.94	
0.22	0.83	0.32	0.89	0.32	0.89			
0.25	0.90	0.52	0.90	0.52	0.90			

COLUMN NO: LL-13		COLUMN NO: LL-14	
TYPE OF SOIL: LUFKIN		TYPE OF SOIL: LUFKIN	
HYDRAULIC GRADIENT: 20		HYDRAULIC GRADIENT: 50	
PORE VOLUME (NONSOAKED)	RELATIVE CONCENTRATION (BROMIDE)	PORE VOLUME (NONSOAKED)	RELATIVE CONCENTRATION (BROMIDE)
0.02	0.81	0.03	0.75
0.07	0.95	0.10	0.94
0.12	0.91	0.18	0.96
0.17	0.92	0.22	0.95